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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDRED AND FIFTY-FIFTH GENERAL MEETING of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, Adelphi, London, on Tuesday, January 9th, 1934, the Chair being taken by Mr. J. McConnell Sanders, Vice-President.

The Secretary read the names of candidates nominated for election and the following list of members elected :—

As Members.—Roy George Parsons, Harold Edward Priston, Conrad Schlumberger, George John Vineall.

As Associate Members.—Patrick Docksey, Sydney Robert Hills.

As Transfer to Associate Member.—Stanley Ernest Blackstone.

As Student.—John Alexander Lindsay.

The following paper was read :—

Oxidation Lubrication, and the Blending of Mineral Oils to obtain Maximum Lubricating Value.

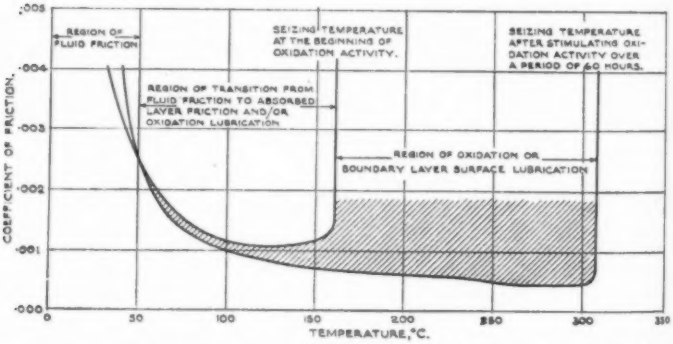
By R. O. KING.

INTRODUCTION.

MINERAL oils, according to present practice, are blended primarily to obtain specified viscosities generally at two temperatures, 70° F. and 140° F., for example. Blends are constituted, therefore, on the assumption that the oil will be used in conditions maintaining a complete fluid film ; separation of the lubricated surfaces, friction and the prevention of wear being dependent on the viscosity of the oil, relative motion of the surfaces and mechanical design, all physical factors. It is well known, however, that in conditions leading to a reduction of film thickness to molecular dimensions, friction and wear are dependent also on an intangible property described generally as " oiliness " possessed by some oils in an exceptional degree. The nature of the lubricating value thus described somewhat unsatisfactorily has become apparent as a result of recent investigations. Hardy,[1] for example, shows that the partial removal of the active (polar) molecules which adhere to surfaces and can, therefore, be removed by passing the oil over clean glass beads or silica chips, decreases lubricating value. A further significant feature is that the residual oil if allowed to stand for a few days at room temperature recovers some of its lubricating value in contact with air, but not if in contact with nitrogen. It appears, therefore, that oiliness or lubricating value depends on the presence in the oil of molecules able to attach themselves

[1]Hardy and Nottage, Dept. Sci. & Ind. Res., " Lubrication Research," Tech. Paper No. 1, pp. 9 and 19.

firmly to a surface or on the formation of such molecules as active products of oxidation, and that Hardy's experimental methods sufficed to demonstrate the latter effect even at temperatures so low that little oxidation activity would be expected. Gilson's experiments with an unloaded and relatively thick oil film subjected to an extremely high rate of shear at temperatures of about 200° C. in an oxidising, and then in a neutral atmosphere, suggested[2] that "the act of lubrication is simply the act of oxidising the oil." Experiments[3] [4] made more recently, but with loaded oil films, run in conditions promoting great oxidation activity extend the results mentioned to show that an unexplored region of high temperature lubrication exists which is dependent on oxidation activity, and on viscosity only in so far as that property may be required as a bridge to reach it. The special lubricating value found to accompany oxidation activity is described hereafter as "oxidation lubrication." The results of the recent experiments are summarised graphically by Fig. 1. The region of nearly



Load on journal bearing 1000 lb./sq. in. of projected area. Air at 160° C. blown into circulated 2-gallon test sample of oil surface speed 11·3 ft. per sec.

FIG. 1.

THE EFFECT OF OXIDATION ACTIVITY ON THE LUBRICATING PROPERTIES OF A BLENDED MINERAL OIL (M.B.).

complete fluid friction in which the effect increases with the increase of viscosity due to oxidation will be seen to extend to a temperature of 50° C. only. Given sufficiently true surfaces and a suitable

[2] Gilson, "Some Bearing Investigations," *General Electric Review* (*U.S.A.*), p. 323, May, 1924.

[3] King, "The Beneficial Effect of Oxidation on the Lubricating Properties of Oil," *Proc. Roy. Soc. A.*, Vol. 139, 1933.

[4] King and Jakeman, "Lubrication in Oxidising Conditions," *Aero. Res. Ctte.*, Rep. & Mem., No. 1517.

degree of viscosity, the oil film may remain unbroken as it diminishes in thickness with rise of temperature, load remaining constant, and seizure postponed until a temperature of about 160° C. is reached. The stimulation of oxidation activity in the oil then imparts special lubricating value or oiliness to the oil and leads to the region of high temperature lubrication extending to over 300° C. in which friction is extremely low, minimum co-efficients of the order of 0·00045 being observed. The oxidation activity required to attain the region of high temperature lubrication leads to the formation of products tending to increase viscosity and therefore fluid friction. The decrease of friction obtained experimentally cannot then have occurred in a fluid film, but must be due to the development of friction reducing boundary conditions. The total oil film thickness, excluding the adsorbed layers, may be regarded as made up of a fluid middle part, in which friction increases with increase of viscosity, contained between boundary layers capable of reducing friction by a greater amount than that due to the viscosity increase in the fluid middle part. The friction reducing property of the boundary layers is explained on the hypothesis[3] that oil molecules in the active state of the early stage of oxidation become attached by their active parts to the metal surfaces and to the inactive part of others already adsorbed. Oxidation activity being sufficient, a load carrying boundary layer many molecules in thickness but decreasing in rigidity in the direction of motion, is built up on each of the lubricated metals to a surface of slip on which motion can occur with little friction. The activated molecules not attaching themselves to surfaces form aggregates by attachment to others and thereby increase viscosity. Thus fluid friction increases in the middle part of the oil film, while the total friction diminishes with the coincident increase of slip on the surfaces of the boundary layers.

The described mechanism of lubrication, being taken as a working hypothesis, indicates that optimum lubricating value in extreme conditions of pressure and temperature, is to be obtained by selecting the constituents of a blend on the basis of oxidation characteristics. Lubrication is frequently required over the temperature range 150° to 300° C., that is in the region of oxidation or boundary layer surface lubrication, Fig. 1. The viscosity of even the heavier mineral oils at temperatures in the upper part of the region approaches that of water at 15° C., and failing the formation of a load carrying boundary layer, with a surface of slip, lubrication would appear to be impossible or extremely defective, accompanied by excessive wear and with seizure inevitable on the application of any considerable load. The building

up of a load carrying boundary layer necessarily of active molecules and of appreciable thickness depends on oxidation processes in the oil, but these are known to be affected also by the nature of the metal of the boundary surfaces. The experiments to be described at present deal only with the bearing of the first mentioned effect on lubricating value.

There is much experimental evidence indicating that the oxidation of oils begins by the direct attachment of a molecule of oxygen to an oil molecule, addition compounds of the nature of peroxides being formed. The compounds are chemically active and promote autoxidation, that is, they act as catalysts to promote the oxidation of substances which otherwise require a higher temperature for the initiation of the effect. Thus a blended mineral oil containing an easily oxidised substance as one constituent, even in small proportion, becomes a suitable medium for autoxidation processes producing activated molecules capable of improving lubricating value, at lower temperatures than would be possible otherwise. Thus a rational basis is obtained for the common belief that blended mineral oils are generally better lubricants than single varieties having the same physical properties. An explanation is also obtained for the variation of the lubricating values of blends having similar physical properties when made up of dissimilar constituents.

It is proposed to describe experiments made with blends and single varieties which appear to confirm the views stated, and lead, therefore, to the suggestion that improvement of the lubricating value of mineral oil blends should be sought for by investigating their oxidation characteristics. The experiments were made in the National Physical Laboratory with the co-operation of Mr. C. Jakeman. The apparatus used and the methods of experiment are described briefly only, in the next section, in view of the more detailed description given when describing experiments dealing in a general way with lubrication in oxidising conditions.[4]

Experimental Method and Apparatus.

The lubrication trials were made using the Jakeman machine, which differs from the familiar Thurston type in that the temperature of the oil film can be raised artificially by a gas flame, and the load remaining constant a seizing temperature is obtained instead of a seizing pressure. The friction falls as the oil film diminishes in thickness with rise of temperature, a minimum value being obtained generally before the seizing temperature is reached and the rotation of the journal stopped automatically. Many lubrication seizures can occur in this way without abrasion of the rubbing surfaces.

The fresh oil feed fitted to the machine was replaced by the circulatory system, shown by Fig. 2, providing for a small quantity, maintained in a state of oxidation activity, to be used continuously for any period. The oil, supplied by force feed from a sump, after passing through the bearing, is in part thrown off the rotating journal as mist and spray into the oxidising mixture of air and hot products of combustion from the gas burner contained in the casing

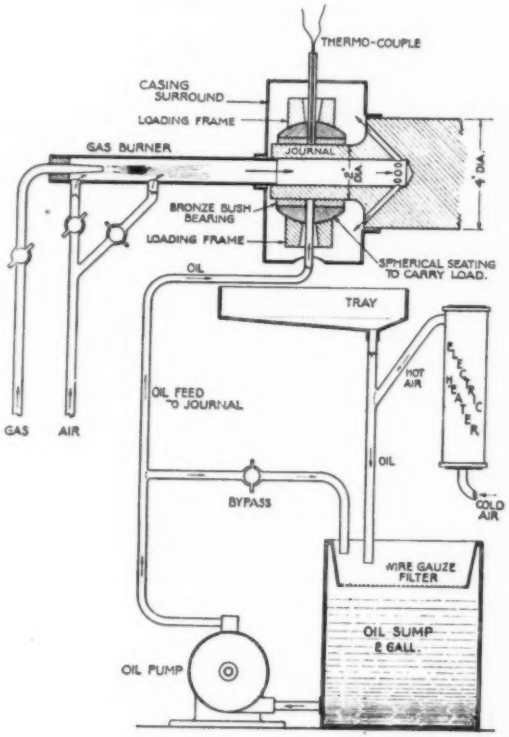


FIG. 2. *Courtesy of the Royal Society*

JOURNAL HEATING AND OIL CIRCULATING SYSTEMS.

surround. The oil running from the surface of the casing is collected in the open tray shown in the figure, and while draining to the sump, is further oxidised by exposure to a stream of air raised generally to 160° C. by the electric heater. The rate of circulation

of the oil varied from about 4 to 30 oz. per minute. A two-gallon sample was used, so on the basis of an average rate of circulation of 16 oz. per minute, the whole sample passed through the testing machine about eight times per hour. The rate of circulation was always in excess of that required for " bath " lubrication and was used to promote oxidation and assist temperature control.

Fig. 2 shows, also, the essential details of the machine other than the devices for applying the load and measuring the friction torque. Referring to the figure, it will be seen that the hot gases from the burner, after passing through the hollow journal, return by the inclined flues in the main shaft to the casing enclosing the journal bearing. The arrangement tends to localise the heating at the journal end of the 4 in. shaft and to ensure uniformity of temperature over the length of the journal. When the temperature of the journal exceeds 250° C., heat conduction along the main shaft is excessive and liable to damage the near roller supporting bearing, not shown in the figure ; nevertheless, the temperature of the journal has been raised to over 300° C. for a short time without apparent ill-effect. A thermo-couple set at the bottom of a small hole drilled into the top side of the bronze bush is used to indicate the approximate temperature of the oil film. The 2 in. diameter nickel chrome steel journal was lapped and polished after being smoothly lathe finished. The bronze bearing bushes were renewed as required, but were always of the same quality, $2\frac{1}{2}$ in. long and the bore 0·0075 in. greater than the diameter of the journal. The load bearing area is small for a new bush, but after " running in " extends over an arc of 80° to 100°. The use of a bronze bush was restricted to a limited period following the attainment of the normal arc of wear. The diameters of the journal and bush were measured, and the arc of wear inspected before and after every trial. When the clearance had increased by 0·012 in. or the arc of wear extended beyond 120°, the bush was rejected.

The experiments were concerned mainly with the performance or lubricating value of oil in extreme conditions of use, that is, when because of a combination of heavy load and high temperature the film between the particular lubricated surfaces becomes extremely thin with seizure imminent. All of the experiments were made with a surface rubbing speed of 11·3 ft. per second and a loading of 1000 lb. per sq. in. of projected journal area, corresponding to a unit loading of 2000 lb. approximately, taken on the normal arc of wear. The performance or useful lubricating value of a particular oil, in the circumstances, load being constant, is taken to be indicated by the coefficient of friction observed

at the temperature of minimum friction, designated hereafter as μ min.. and the somewhat higher temperature at which, owing to a further decrease of film thickness, seizure actually occurs. The letters S.T. will be used hereafter as an abbreviation of seizing temperature. The trial of a particular oil was continued as long as marked changes of μ min. and S.T. were observed, and required the use of the testing machine for daily runs of about $7\frac{1}{2}$ hours, over a period of 1 to 2 weeks. A complete set of friction observations at temperatures over the range 40° to S.T. was taken daily.

The experiments were begun with the bronze bushes lathe bored, using a broad finishing tool. The surface obtained, described hereafter as an " A " surface, was without measurable effect on the performance of high viscosity oils used at relatively low temperatures. When, however, the performance is expressed in terms of μ min., and therefore at temperatures approaching that of seizure, the oil film is extremely thin, and, apart from special oxidation lubricating value, the friction observed is made up of fluid friction varying over the bearing surface with variations of film thickness and adsorbed layer friction varying with high spot area which changes in extent with wear. The mixed friction region for oil of the viscosity of M.B., in the load and speed conditions of the trial, extends over the temperature range 50° to 160° C. Lubrication trials, when made at relatively high temperatures, generally yield inconsistent results and usually end with seizure in the mixed friction region, especially when the feed to the journal bearing is of fresh oil not in a state of oxidation activity. The region can be passed through without seizure and that of oxidation lubrication attained when starting with fresh oil, only by maintaining the fluid film unbroken, while oxidation activity is promoted. Thus the region of high temperature oxidation lubrication was not attained until the bronze bearing bush was provided with a smooth and true surface. The most effective surface was obtained by " running in " the journal bearing surface with castor oil containing lead tetra ethyl in the small proportion of 7 c.c. per gallon. The experiments described in section (3) were made with highly finished surfaces except when the " A " surface is mentioned.

The physical properties of the mineral oils used for the experiments described in section (3) are given in Table I. below. Oil M.B. is a proprietary blend, the proportion and nature of the constituents being unknown. Oil M.B. 2 is a known blend containing 40 per cent. of " bright stock," 30 per cent. of a paraffin base distillate and 30 per cent. of an asphaltic base distillate. Oil C.S. is refined from the residuum from the distillation of

Pennsylvania crude oil and is generally known as " bright cylinder stock." Oil R.N. (No. 1 Russian) is a distillate from what is generally regarded as a naphthenic base crude, and V.A. is also a distillate but procured from an asphaltic base crude. Oils R.N., C.S., V.A., are typical varieties commonly used to make up blends having properties considered desirable for the lubrication of aero engines.

TABLE I.

Physical Properties of the Oils.

	M.B.	M.B.2.	C.S.	R.N.	V.A.
Sp. gr. at 60° F. ..	0·905	0·9105	0·891	0·909	0·937
Closed flash point ..	430° F.	440° F.	505° F.	385° F.	445° F.
Redwood vis. 70°F.	2164 secs.	2301 secs.	6800 secs.	1290 secs.	4105 secs.
Redwood vis. 140°F.	216 secs.	226 secs.	550 secs.	133 secs.	260 secs.
Redwood vis. 200°F.	72 secs.	74 secs.	150 secs.	53 secs.	75 secs.
Pour test (A.S.T.M.)	25° F.	20°–25°F.	20° F.	0·8° F.	10° F.

LUBRICATION TRIALS, BLENDS AND SINGLE VARIETIES.

Experiments with the blended oil M.B.—The graphs, Fig. 3, show the improvement in lubricating value of oil M.B. during a running time of 61 hours, oxidation activity being maintained during the period. The seizing temperature was then in excess

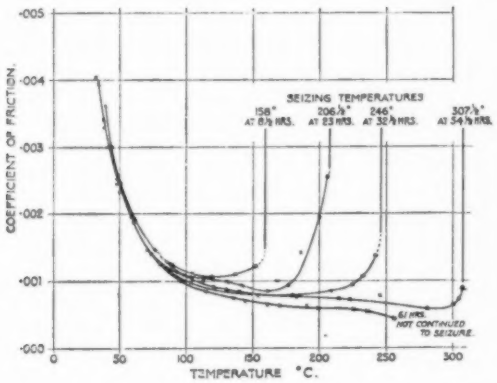


FIG. 3. *Courtesy of the Royal Society.*

RISE OF SEIZING TEMPERATURE AND DECREASE OF FRICTION WITH TIME IN USE. OIL M.B. LOAD ON JOURNAL BEARING 1000 LB./SQ. IN. OF PROJECTED AREA. AIR AT 160° C. BLOWN INTO CIRCULATED 2-GALLON TEST SAMPLE OF OIL.

of 307° C., and the oil was emitting smoke and steam profusely. The cloud rising from the journal bearing at the lower temperature of 250° C. (482° F.) is shown by the photograph, Fig. 4.

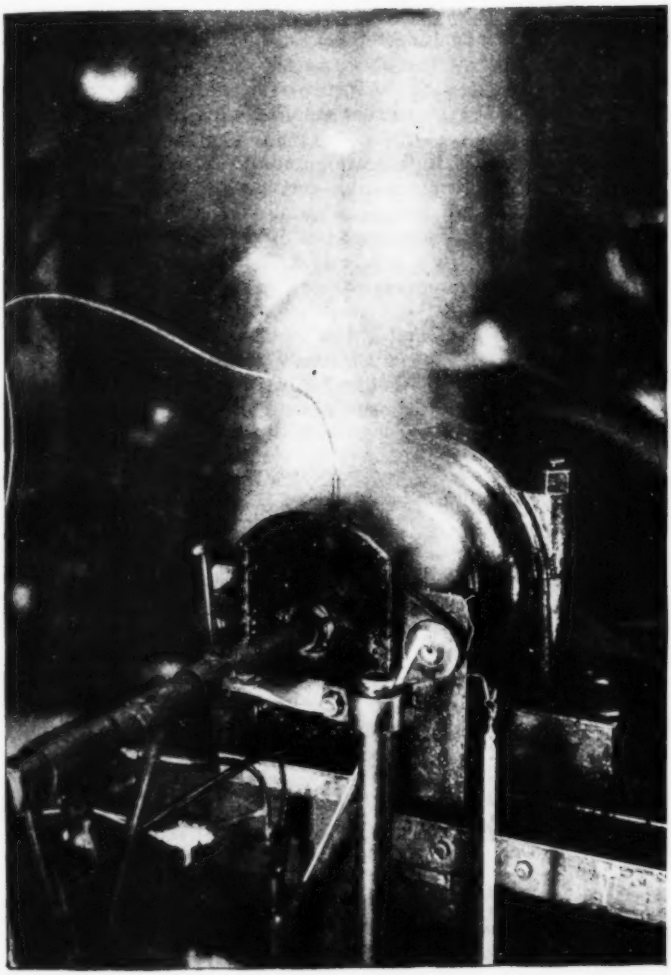


FIG. 4. *Courtesy of the Royal Society.*

SMOKE AND STEAM (OXIDATION PRODUCTS) RISING FROM JOURNAL BEARING RUNNING WITH LUBRICATING OIL FILM AT 250° C. (482° F.).

The testing machine was not designed to run at oil film temperatures higher than 250°, even for short periods, and the trial was continued at lower running temperatures. The temperature was, however, raised daily to 260° C. in the expectation that in the severe conditions seizing temperature would fall soon to an observable value, but a further running time of 100 hours was required before this occurred. The relatively low value of 137° C. then observed seemed to indicate an accidental condition, because on continuing the trial, seizing temperature rose rapidly and friction diminished in the manner observed when the oil was fresh. The trial was discontinued at 197½ hours while lubricating value as determined by μ min. and S.T. was improving, although the oil was heavily impregnated with oxidation or decomposition products.

Observations of μ 40° and μ min. made during the period 54½ to 156 hours, while seizing temperature was too high to be observed safely, are given in Table II., and it will be seen that lubricating value as shown by the coefficient of friction varied irregularly.

TABLE II.

M.B. Oil Trial, Load 1000 lb./sq. inch, speed 11·3 ft. per sec., bush "run in" on doped castor oil.

Time hours.	Running Temp.	μ 40°.	μ min.	Temp. of μ min.	S.T.
54½	180	0·0035	0·00055	285°	307½°
61	185	0·00315	0·00045	255°	
68½	160	0·0033	0·00055	250°	Seizing
71	—	0·00375	0·00070	226°	temperature
78	185	0·0035	0·00050	255°	too
87	210	0·0035	0·00070	260°	high
95	185	0·00355	0·00055	250°	to be
102	190	0·0034	0·00055	255°	observed
105	—	0·0036	0·0005	250°	with
111	190	0·00365	0·0005	255°	safety.
118½	210	0·0038	0·00065	255°	
125½	150	0·00375	0·00075	250°	
132½	195	0·0037	0·0005	250°	
140	180	0·0038	0·0005	255°	
142	—	0·0036	0·0005	250°	
149	175	0·00375	0·00045	255°	
156	195	0·0040	0·00075	255°	

Variations of friction at the relatively high temperature of the minimum value are attributed to variation of oxidation activity, but might be regarded as due to accidental changes of surface smoothness of the bronze bush. The latter explanation does not suffice, however, for the irregular changes of μ 40° observed necessarily when the oil film is of sufficient thickness for surface imperfections to be of minor importance. The changes of friction

at 40° will, therefore, be considered and can be explained as depending on three factors :—

(*a*) An increase of fluid friction as oxidation products accumulate during the course of the trial and increase viscosity.

(*b*) A decrease of friction due to oxidation activity. The effect is of a residual nature, the recorded magnitude depending on the interval of time between activation and the taking of observations.

(*c*) A decrease of fluid friction following from the breaking down of molecular aggregates with the effect of decreasing viscosity, during the late stage of oxidation reached at the higher temperature of the trials. The effect is permanent, depends on time of exposure to the extreme conditions of the trials and indicates the end of the oxidation lubrication life of the oil.

The considerations mentioned lead to the conclusion that the oxidation lubrication value of a blended oil especially is dependent on its history as well as on the nature of the constituents. Thus oxidation activity can be induced readily in a fresh oil containing unsaturated compounds and in suitable conditions the process will continue by autoxidation, the oil improving in oxidation lubrication value although not used, an effect which has been observed but not made the subject of special experiments. The effect is analogous to the well-known tendency, now attributed generally to peroxidation, of the lighter oils used as fuel to form gum on standing when the constituents are in part unsaturated compounds. When, on the other hand, an oil has been used in severe conditions for a period so long that the more easily affected constituents have passed through the early stages of oxidation, greater oxidation stimulation would be required to improve lubricating value, and the effect would diminish on the withdrawal of activation. M.B. oil, for example, failed to retain, on standing, the exceptional oxidation lubrication value stimulated during the course of a long trial. Thus a fresh sample of the oil which attained a performance represented by a μ min. of 0·0005 and a S.T. of 309°, on the completion of 40 hours' activation, when used again after standing for two months was found to have lost about 50 per cent. of oxidation lubricating value, μ min. being 0·0008 and S.T. 235°. The process of improvement began anew on continuing the trial, but proceeded less rapidly than when the sample was fresh.

The single variety oil, R.N.—The double effect of oxidation, namely, to form partial oxidation products initially and to break down molecular aggregates in the later stage, has been mentioned. When the blended oil M.B. was used for trials the first mentioned effect was especially evident and long lived, and the accompanying oxidation activity led to an improved lubricating value maintained

over a period of corresponding length, which tended to mask the deleterious effect of the breakdown of molecular aggregates. The two effects are, therefore, difficult to distinguish during trials with oil M.B., but their incidence is clearly evident in relatively short trials of oil R.N. Visible oxidation products were not formed in the conditions of the trials, and viscosity as indicated by the value of μ 40°, after a short period of increase, diminished with the progress of oxidation. Trials of the oil, conducted at relatively low running temperatures, and using an "A" surface bush, show an initial improvement of performance with the progress of oxidation; μ min. diminished from 0·00125 to 0·0009 and S.T. increased from 73° to 163°, over a period of 71 hours' running. The improved performance was not maintained on continuing the trial, and at 88 hours' μ min. had increased to 0·0010 and S.T. had fallen to 134°. The significant feature of the trial, in respect of oxidation effects is that μ 40°, dependent mainly on viscosity, ceased to increase with the progress of oxidation immediately following the attainment of the optimum performance. That is, on exceeding 71 hours' exposure of the oil to the oxidising conditions, the further increase of viscosity is balanced by the diminution due to the breakdown of molecular aggregates, an effect indicating the advent of the final stage of the life of the oil as a lubricant.

TABLE III.

Oil, R.N., showing change in lubricating value during Trials of Fresh and Pre-oxidised samples.

	Pre-oxidation time.			
	Fresh oil.	10 hours.	20 hours.	30 hours.
S.T. change ..	+90°	+54°	+29°	—17°
μ min. change ..	—0·00035	—0·00020	—0·00020	0·0
μ 40° change ..	+0·0006	+0·00045	0·0	0·0
Time required ..	71 hours.	61 hours.	26 hours.	7 hours.

The oxidation lubrication life of fresh R.N. oil in the running conditions of the trial described, extending over a period of about 71 hours only, would be expected to depend, therefore, to a notable degree on the oxidation history of the oil prior to use as a lubricant. The pronounced effect of oxidation history was confirmed by lubrication trials of three samples of oil R.N. submitted to varying periods of oxidation before being used in the testing machine. The samples taken in turn were pumped from a sump maintained at 70° into the throat of a small venturi through which air heated to 165° was blown by a compressor. The oil mist and spray discharged into a closed iron cylinder, draining back to the sump for recirculation. The oxidising conditions, especially in respect of the spraying of the oil, were more severe than during lubrication

trials, but visible oxidation products were not formed. A sample oxidised for 10 hours scarcely changed colour. Oxidation for 20 hours effected a change from the original straw colour to a light brown, and for 30 hours to a deep red. The significant changes of S.T. and friction, observed when the pre-oxidised samples were submitted to trial, are given in Table III. The similar changes observed during the trial of fresh oil are included. The plus sign indicates an increase and the minus sign a decrease of the values observed over the stated times.

The experimental results given in Table III. show the extent of the reduction of the oxidation lubricating life of the oil by the pre-oxidation treatment. Thus, when a sample of the oil was pre-oxidised for a short time longer than 20 hours the oxidation lubrication value was completely exhausted, and the performance of a 30-hour sample deteriorated as from the beginning of the trial in the testing machine. A permanent deterioration following immediately the attainment of an optimum lubricating value appears to be characteristic of oil R.N., and after a relatively short period of use in oxidising conditions the oil becomes an inert fluid in which oxidation lubricating value cannot be stimulated.

The described oxidation lubrication effects for oil R.N. were obtained when running temperatures did not exceed 100° C. and the oil was used to lubricate an "A" surface bush. Similar effects were observed in relatively small degree only when higher running temperatures ranging from 150° to 180° became possible on improving the lubricated surfaces, see Table IV. below.

TABLE IV.

Trial Results Oil R.N., Fresh Sample.

Time hours.	Running Temp.	μ 40°.	μ min.	Temp. of μ min.	S.T.
395	—	—	—	—	—
401	—	0·0027	0·0005	160°–170°	184
408	170	0·0025	0·00055	160°–185°	220
414	170	0·0029	0·00055	150°–190°	225
417	—	0·0029	0·0005	150°–190°	223
424	180	0·0029	0·0005	150°–190°	230

The experimental results given in Table IV. may be taken to show that oxidation activity at the higher temperatures is not of a type to improve the lubricating value of oil R.N., or that the consequent improvement was exceptionally short lived, occurring mainly during the few hours of the trials preceding the first observation of μ and S.T. Either view is supported by the slight variation of μ 40° during the trials, taken as showing the absence of the viscosity increase that during the earlier trials of oil R.N. accompanied an increase of oxidation lubrication value.

The single variety oil, C.S.—The basic variety C.S. possesses an exceptionally high viscosity and greater resistance to oxidation than other mineral oils, according to oxygen absorption tests. When the running temperature during lubrication trials was not higher than 100°, performance in terms of μ min. and S.T. remained unchanged during a trial period of 54 hours, but μ 40° increased from 0·0047 to 0·0054 indicating an oxidation effect of some sort, tending to increase viscosity. A fresh sample of the oil, when used for trials made at relatively high running temperatures, improved in lubricating value with the progress of oxidation, μ min. diminishing from 0·0010 to 0·0008 and S.T. rising from 161° to 235° during 20 hours of use, but μ 40° *diminished slightly*. The same sample used two months later exhibited a substantially invariable performance in respect of μ min. and S.T., but μ 40° tended to *increase*.

A synopsis of the trial results for oil C.S. is given below. The colour of the oil remained unchanged during the trials made at a running temperature of 100°, but visible oxidation products formed in the oil during the later trials when running temperatures ranged from 130° to 175°, and were raised at daily intervals to over 200° to induce seizure. The trial periods were too short to determine the effect of oxidation on the life of the oil.

TABLE V.

Trial Results Oil C.S.

Time hours.	Running Temp.	μ 40°.	μ min.	Temp. of μ min.	S.T.
	(*a*) Fresh sample used with an " A " surface bush.				
2	100	0·0047	0·00125	122	141
26	100	0·0053	0·0012	110–122	132
54½	100	0·0054	0·0013	118–130	145
	(*b*) Fresh sample used at high running temperatures.				
2	—	0·0060	0·0010	140–150	161
9	130	0·0057	0·00095	140–185	218
19	—	0·0056	0·0008	160–215	235
25	170	0·0058	0·0008	160–190	227
45	175	0·0058	0·0008	165–190	221
	(*c*) Same sample run two months later.				
9	150	0·0053	0·0008	150–230	257½
16	150	0·0058	0·0008	150–235	256
30	165	0·0056	0·0007	155–230	257½

It will be seen, by reference to Table V., that oxidation at the relatively high temperatures of the later trials, (*b*) and (*c*), effects an irregular *decrease* of μ 40°, attributable to the decrease of viscosity due to the breakdown of molecular aggregates being greater than the increase due to oxidation. The defect of oxidation activity of the type causing an increase in viscosity, when the oil is used at high running temperatures, accounts for the relatively high values

of μ 40° and the small improvement of performance in terms of μ min. and S. T. as compared with that obtained when using the blended oil M.B. The explanation is supported by the measured overall viscosity changes of the oils. The viscosity of oil C.S. taken at 200° F. was 150 Redwood seconds when fresh, and had reverted to the same value after the high temperature trials (*b*) and (*c*), whereas the viscosity of oil M.B. increased in similar circumstances, from 72 to 85 Redwood seconds The results of trial (*a*), made at relatively low running temperatures, appear to be inconsistent with the explanation because the definite increase of μ 40° then obtained, although indicating oxidation activity of the type increasing viscosity, was not accompanied by an improvement of performance in terms of μ min. and S.T. The reason is probably that the first mentioned trials were made with an "A" surface bush, which led to rupture of the oil film at lower temperatures than required to obtain oxidation lubrication in oil C.S.

The single variety oil V.A.—The performance of the asphaltic base oil V.A. was inferior to that of C.S. when trials were made using "A" surface bushes ; but the two oils were found to be of nearly equal merit, in terms of μ min. and S.T. when on improving the surface of the bush, trials could be made at high running temperatures. Trial results are given below.

TABLE VI.

Oil V.A., Fresh Sample, Bush No. 32.

Time hours.	Running Temp.	μ 40°.	μ min.	Temp. of μ min.	S.T.
424½	—	—	—	—	—
430	—	0·0042	0·0008	130–160	176
435	160	0·0045	0·0008	140–170	213
438	—	0·0046	0·0008	140–185	206½
445	140	0·0047	0·0007	140–190	195½
452	155	0·0043	0·00075	150–210	225½

TABLE VII.

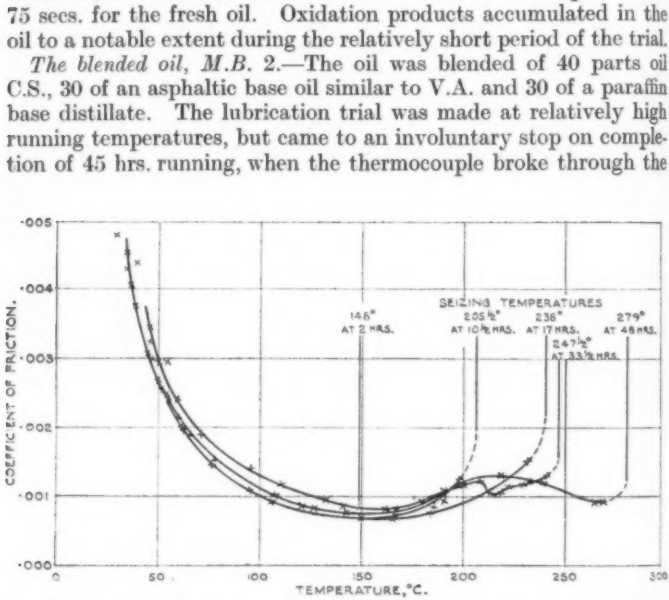
Oil C.S., Fresh Sample, Bush No. 32.

Time hours.	Running Temp.	μ 40°.	μ min.	Temp. of μ min.	S.T.
452	—	—	—	—	—
454	—	0·0060	0·0010	140–150	161
461	130	0·0057	0·00095	140–185	218
468½	140	0·0055	0·0008	160–185	219½
471	—	0·0056	0·0008	160–215	235
477	170	0·0058	0·0008	160–190	227
484	180	0·0058	0·0008	140–190	230½
490½	175	0·0059	0·0008	165–180	215½
497	175	0·0058	0·0008	165–190	221

Referring to the tables, it will be seen that the improvement of the lubricating value of oil V.A. with the progress of oxidation

is the same approximately as that observed for oil C.S. The trial of oil V.A., carried on for a running period of 28 hrs. only, was discontinued before the effect of oxidation on the life of the oil was determined fully. A sudden diminution of μ 40°, Table VI., occurred after 21 hrs. running, however, and the Redwood viscosity of the used oil measured at 200° F. was 74·5 secs. as compared with 75 secs. for the fresh oil. Oxidation products accumulated in the oil to a notable extent during the relatively short period of the trial.

The blended oil, M.B. 2.—The oil was blended of 40 parts oil C.S., 30 of an asphaltic base oil similar to V.A. and 30 of a paraffin base distillate. The lubrication trial was made at relatively high running temperatures, but came to an involuntary stop on completion of 45 hrs. running, when the thermocouple broke through the



Load on journal bearing 1000 lb./sq. in. of projected area. Air at 160° C. blown into circulated 2-gallon test sample of oil. Surface speed 11·3 ft. per sec.

FIG. 5.

RISE OF SEIZING TEMPERATURE AND DECREASE OF FRICTION WITH TIME OF USE. OIL M.B.2.

bronze bush and fouled the journal. Temperature and friction observations for the period run are given graphically by Fig. 5. The S.T. was rising when the trial was discontinued and the maximum for the blend was therefore not determined, but the rate of increase with time of running and oxidation was substantially the same as that observed for the blend M.B., which ran to a S.T. of over 300° in the same conditions. A feature of the trial illustrating the effect of autoxidation is that the blend of the high viscosity and not easily oxidisable oil C.S. with two inferior

varieties attains a S.T. of 279° after 45 hrs. of use and oxidation, whereas the maximum observed during a trial of C.S. alone was 235°. The two trials were run in the same conditions and with the same bronze bush, the trial of oil M.B. 2 following immediately after that of oil C.S. It is apparent from an inspection of the curves, Fig. 5, that oxidation activity is deficient over the temperature range 150° to 220° leading to a tendency to seizure indicated by friction increasing as the temperature rises. Oxidation activity over the higher range 220° to 270°, however, suffices to reduce the tendency to seizure, friction falling as the temperature rises. The blend requires the addition of a constituent adapted to promote oxidation activity over the lower range of temperature. Comparing Fig. 3 with Fig. 5, it will be seen that oxidation activity in the blend M.B. is of more nearly uniform effect over the temperature range 150° to 300°. The attainment of optimum performance in trials of either blend requires oxidation for a running period of the order of 50 hrs., when made up of daily runs of about 7½ hrs. The same effect would be expected in a shorter period of continuous running in the same conditions. The ability of blends containing constituent oils of dissimilar oxidation characteristics to run as lubricants in more severe conditions than single varieties is attributed to the possibility of maintaining oxidation activity by autoxidation in such mixtures to a greater extent than in single varieties.

Conclusions Supported by the Experiments with Blends and Single Varieties.

The oxidation behaviour of the single varieties of oils used for trials at high running temperatures is significant in that the degree of improvement of lubricating value with the progress of oxidation is slight and persists for a relatively short time. Furthermore, viscosity increases with use and oxidation for a short period only, then diminishes and does not recover the former higher value on further oxidation.

The overall viscosity changes of the single varieties and the two blends during the trials described are shown by " before and after " measurements given below.

Table VIII.

Viscosities of Oils before and after Lubrication Trials Redwood Seconds.

Oil.	Viscosity at 140° F. Fresh.	Used.	Viscosity at 200° F. Fresh.	Used
M.B. ..	216	290	72	85
M.B.2 ..	226	280	74	83
R.N. ..	133	140	53	54
C.S. ..	550	568	150	150
V.A. ..	260	279	75	74

The measurements indicate that the single varieties, after the oxidation time of the trials, do not increase in viscosity with further oxidation except at relatively low temperatures, and that at temperatures exceeding 200° F. (93° C.) a decrease of viscosity would be expected. The measured viscosity changes accord, therefore, with the observed tendency of μ 40° to decrease during the later stages of the lubrication trials of these varieties, made at running temperatures ranging from 150° to 200°. Furthermore, the failure of oxidation activity to increase or maintain viscosity is concurrent with a failure of performance to improve with continued use and oxidation. The viscosities of the blended oils M.B. and M.B. 2, on the other hand, continue to increase or at least are maintained at an increased value over relatively long periods of oxidation, while performance improves and remains at the higher level attained. The oxidation behaviour of the blended oils is attributed to autoxidation. Thus, the lubricating value of a blend of a high grade oil not easily oxidised, such as C.S., with other oils tending to oxidise at relatively low temperatures, may be greater than that of the better constituent used alone. The effect depends on autoxidation, that is oxidation of the better constituent promoted by the active oxidation products formed more readily in the inferior one. The blending of oils for optimum performances in oxidising conditions is dependent, therefore, on a selection of constituents to maintain the necessary oxidation activity in the blend over the range of temperature required in use. A method of selection is indicated by the effect of oxidation on change of viscosity, but requires development by further experiments to relate changes of viscosity in conditions promoting oxidation to change of lubricating value in the same conditions.

The attainment of the state of oxidation lubrication would be expected to prevent wear of the bronze bush even in the severe conditions of the trials. Measurements made before and after using oil M.B. indicate that the metal of the bush tended to flow rather than to wear. On the other hand, when the degree of oxidation lubrication was slight or non-existent as in trials with oil R.N., the wear of the bush was pronounced.

The experiments described were not made for the purpose of showing that mineral oils should be blended according to oxidation characteristics. Had that purpose been in view, more complete evidence might have been obtained. The significance of the experimental results may, however, be enhanced by their not having been obtained with the object of supporting a particular hypothesis.

DISCUSSION.

The Chairman (Mr. J. McConnell Sanders) said the members were indebted to Capt. King for providing them with a very interesting and provocative paper. They were living now in a very interesting period of lubrication history. Not only were new methods of refining coming into being, but new conceptions of the value of the components of lubricating oils, and new conceptions of the whole mechanism of lubrication, were developing. Therefore Capt. King could be looked upon as a pioneer in presenting those new conceptions to the members' attention, and no doubt they would be interested in discussing and ventilating the various points which arose in connection with the matter.

Personally he would like to ask the author if he had considered the effect of boundary layer formation of components in the oil, which, while not being oxidised products, might still contain active or polar molecules. He was thinking more particularly of sulphur compounds, which differed very considerably, both in quality and quantity, amongst the various types of lubricating oils. It might perhaps be the case that oxidising conditions affected the activity of pre-existent sulphur compounds, more especially as regarded their eventual action on certain bearing metals.

As a chemist, he would have liked to see the various oils used in the experiments characterised by their chemical qualities, as well as by their physical characters. For instance, the degree of unsaturation, the sulphur content and the nature of the hydrocarbon components would have been of great interest; and if the analysis of the oil before and after the experiments could have been included, the value of the paper would have been considerably increased.

Then again, he should like to have had a little more information with regard to the experimental evidence of the existence of oxidation products. The members were told throughout the paper that visible oxidation products were frequently absent. How were the invisible products indicated or estimated ?

Reference was made occasionally to colour changes, but colour changes, under the conditions of test, might not necessarily be due to the oxidation compounds formed, but to metallic compounds or to colloidal suspensions of finely divided metals in the oil, and since it was known that the products of combustion of the heating flame were entering into the oil and not removed in the process, surely colour changes might be due partly to components present in the gas supplying the burner, or to their action on the metal.

Finally, he would like to ask the author, on behalf of motorists interested in lubricating oils, whether it would be better not to

renew the oil in the engine sump but simply to add a small quantity of an easily oxidised oil to the already used one ?

Col. S. J. M. Auld thought Capt. King's paper was definitely one of the big advances which had been made in the study of lubrication. He was not going to discuss Capt. King's theory or his practical results. The theory had obviously yet to be developed to cover all the points which could be raised in connection with it, and it would not be difficult to raise purely hypothetical objections in certain directions. On the practical side Capt. King was obviously too fine an experimentalist to have missed any of the points which might occur to one, such as the need for having comparative values, control and measurement of the extent of the oxidation, and so on.

His chief feelings on reading the paper through had been along rather different lines. Most of the members present would recollect that whilst he was in Kensington Gardens, Peter Pan held a conference of the various birds on the subject of nest building, and after one of his cogent but somewhat whimsical explanations the birds said : " Now we know why we build our nests like that." His first feeling had been one of gratitude to Capt. King for explaining to the members why they built their lubricating oils " like that," because most of the things which Capt. King had shown them were matters of known practice and were appreciated properties of lubricating oils. There was in the naphthenic base oil—in the Russian—that lack of " guts," should he say, which was generally ascribed to those oils ; there was in the asphaltic base oil good lubricating value, but poor condition ; there was in the paraffin base oil, as typified by the Pennsylvanian stock, that rather unbending superiority which those grades were presumed to have ; and, lastly, but by far the most important, there was, for the first time, a really well supported hypothesis, supporting in its turn the belief of many of the members, and which had been applied in certain quarters for a long time past, that blending of selected stocks was not merely a means factitiously of producing a lubricating oil possessing certain physical constants, but was a means of producing an oil of definitely better lubricating value.

But once those points had sunk into his mind, he had not been quite clear what came next, or what really had been gained, other than a big step forward in the understanding of the behaviour of lubricants. As petroleum technologists they were looking for possible and ultimate improvement of oils, but he took it that there was not in Capt. King's mind any suggestion, at any rate in the meantime, of merely looking for a fresh " dope " for improving lubricating oil by use of oxidation products. But he did take it

from the words in Capt. King's peroration that there was just a possibility in the author's mind of using the results of his experiments as a means of characterising oils. Specifications were very fashionable, and they were very useful, but they equally definitely could be abused. There was just the possibility of the danger, in a case of this kind, of other people looking at the results and of reading into them too much and attempting to build up methods of characterising lubricating oils which were not justified by the results. It had to be remembered that these experiments related primarily to very high temperatures. It was boundary lubrication, and the big bulk of practical lubrication occurred within the fluid friction region. Moreover, there were all sorts of other characteristics of oils which were required. If it were merely lubricity or oiliness which was wanted, he supposed many of the members would be concerned in growing castor oil seed instead of being in the petroleum industry, and there were all sorts of things apart even from that. Capt. King had himself pointed out that viscosity was an essential bridge to this region of oxidation lubrication, and personally he was not quite clear whether the big bulk of the lubrication in which the members were interested was so seriously going to be affected by the conditions which apparently were existent at those very elevated temperatures. Lubrication at those high temperatures was, fortunately, a comparatively rare occurrence, but it did occur and it had to be met. Although he would hate to be thought to be in opposition in any sense to the really wonderful work which the paper indicated had been done, he did feel that there might be other things concerned with high temperature lubrication, such as what medical men called the "presentation" of the oil to the lubricated surface. For example, he had had an idea that just a partial carbonisation might actually maintain, or help to maintain, the oil film, and actually keep it there under conditions of high temperature lubrication. He did not know whether high temperature lubrication had been studied, or, for that matter, thought of in terms of alteration of other basic physical properties as distinct from the chemical ones—things like surface tension and so on—at those high temperatures.

It was for that reason that he would like to put in a word of warning against using the results immediately as a means of characterising oils. The theory had a big field in front of it for developing something that students of lubrication perhaps did not have in their hands at present. On the other hand, he did not doubt that, for a long time to come, the real test of lubricating oil was going to be in the engine. He asked those present not to imagine that he was being reactionary. He desired to subscribe his opinion that they had been listening that night to something

which was really of very first importance in the study of lubrication.

Mr. C. H. Barton remarked that in some ways these results of oxidation lubrication reminded one of the properties of extreme pressure lubricants, but there was this difference—that extreme pressure lubricants possessed their properties at low temperatures; extreme pressure lubricants had the property of carrying very high bearing pressures at temperatures below 100° C., whereas in the case of the lubricating oils which Capt. King had examined the special properties did not show up until very high temperatures were reached.

It had occurred to him that it might be of interest to examine the load carrying properties of oils under oxidising conditions. In Capt. King's experiments apparently the bearing loads were kept constant, as well as the rubbing speeds, and only temperatures were varied. It would be interesting to know the effect of raising the bearing loads in order to see whether the oxidation of the oils increased their load carrying capacity.

He also wondered whether oxidation lubrication properties could have any effect except in, say, internal combustion engines. After all, ordinary bearing temperatures very rarely exceeded 100° C.

Dr. E. R. Redgrove said the author was to be congratulated on having given the Institution an opportunity of hearing and discussing a paper dealing with lubricating problems which, so far, had received but scant attention. He referred to the useful life and the seizing temperature of an oil. Those who had been intimately connected with the practice of lubrication must, at some time or another, have encountered baffling problems which seemed to be due only to sheer cussedness on the part of the oil or machine; all knew of some of the surprising results which had been obtained by Stanton, of the investigation of the cause by Hardy and Miss Nottage, and it would seem that at last they were on the point of emerging from a fog of mystery into the sunshine of scientific facts.

The theory which had been advanced by the author (and he thought they might go so far as to call it the theory of diluted oxidation) must be treated with the greatest care; the caution which was given in the concluding paragraph of the paper was very timely, because some misguided but well-meaning oil blender might produce some awful concoction, based entirely on oxidising properties, which would be disastrous to the engines it was intended to lubricate.

In the tests which had been described that night, the oils had

been subjected to most strenuous conditions, during which time they had been in part distilled, polymerised, cracked and oxidised ; and, further, it must be remembered that to no small degree, reducing actions were playing a considerable part in the chemical changes which were taking place. The oxidation of the higher boiling fractions, and particularly of the residual stocks, generally proceeded along entirely different lines from those which operated when the lighter distillates were oxidised, and it was quite feasible that a solution of the oxidation products of the latter in those of the former would impart some beneficial properties without any of the disadvantages which were usually associated with lubricating oil decomposition.

Some years ago he had been investigating certain properties of lubricating oils after they had been subjected to oxidising conditions, and he had obtained results which definitely pointed to the same conclusions as those arrived at by the author. The oxidation of the oils had been carried out in the Air Board apparatus, and the static friction of the oxidised oils had been determined on a special apparatus, which was illustrated by a slide.

By a series of slides he showed that the static friction of oxidised lubricating oils, when freed from any hard asphalt which might have been formed, was lower than that of the unoxidised oils. The friction/temperature rise of the fresh oils was entirely eliminated, and the reduction in friction for oils blended from a distillate, and a refined residual stock was greater than for a straight distillate alone. Medicinal paraffin formed practically no asphalt, but a large amount of acidity, and there was a correspondingly big drop in the coefficient of static friction.

It was thus seen that confirmation of the author's conclusions had been obtained independently by entirely different methods, and when much more work on the subject had been concluded there was reason to hope that the " art " of the oil blender would be replaced by a well founded science.

Mr. E. A. Evans said the author had not given the slightest clue in the paper as to how long the work had taken, neither had he given any idea how the bearings were produced. Personally, he imagined that the surfaces had taken a very long time to prepare. Capt. King just mentioned the fact that the final running in was given by a dose of castor oil with a little ethyl, but he gave no indication why. It would be interesting to know why that curious combination should be applied. The author had certainly given the members a good deal of food for thought. He stated that oxidised oil did have a definite benefit in reducing the coefficient of friction. He had shown, too, that there was a stage at which the optimum oxidation was obtained, after which its effect became somewhat

deleterious, or at least did not improve. It seemed to him that Capt. King had just taken the members to the end of Chapter I, and that the beginning of Chapter II would deal with the subsequent period after the optimum zone had been reached. Could the author suggest a means to check the oxidation at that particular point ? Chemists had definitely come to a particular stage in the outlook of lubrication where their old-fashioned views had got to change, and contributions of the kind of Capt. King's were of the utmost value. Personally he was not quite sure whether he agreed with those people who had very modestly suggested that they were not much concerned with the very high temperatures. Surely they are of extreme importance. Capt. King is associated with the Air Ministry. In the development of aero-engines high temperatures were becoming more and more important, especially the high temperatures on the top piston ring. The biggest nightmare of a pilot was a gummed ring, and anything which would help to solve the possibility of a gummed ring, and ultimate seizure, would be an enormous advance in the mechanism of lubrication. We are naturally faced with the problem of fashion in specifications, but that must not deter us. We are faced with the problem of people asking : " When shall we change an oil ? Is it safe to go on using it ? " That is a question which could not be answered satisfactorily. He said that perfectly honestly.

Dr. W. R. Ormandy remarked that there had been a time not very long ago when it was customary to state, and to accept the statement when made, that stable oils were what was required, oils that would not oxidise readily, and which would remain lubricating oils over a wide range of temperature. It had been stated, and many had believed it, that the presence of sulphur was obnoxious, because sulphur meant in reality that the oil with which it was associated was unstable, and it was because there was low sulphur in Russian oils and low sulphur in Pennsylvanian oils that those oils gave better lubricants than the oils from which asphalt was produced, which contain considerable amounts of sulphur. Now, it was said that the best thing to do was to mix one of those really high flash-point stable oils with one which oxidised readily and, as an explanation, the statement was made, if he understood the paper correctly, that the unstable oil was oxidised or peroxidised ; that is, it had got free linkages or free fields of action which took up oxygen, and it was the oxides or oxidised bodies which in some mysterious way brought about the oxidation of the rest of the low-grade oils and had an effect on the large bulk of the high-grade oils.

Judging by the steam being evolved, as shown in the picture of the working plant thrown on the screen, there was something

radical going on. Yet their late lamented friend Mr. Hoblyn had introduced a test for lubricating oils wherein the oil in a small porcelain was heated in the presence of air to temperatures of the order of 250° C., and had showed that those oils stable to 20 or 30 hours of heating, when examined under the microscope, were free from asphaltic bodies. They gave a homogeneous field under the microscope. But the unstable oils, at the end of the same period, or in a much shorter period, showed, under the microscope, the presence of gradually increasing numbers of small particles of what, on analysis, afterwards proved to be a mixture of hard and soft asphalts. It was very difficult to understand the oil being oxidised at this rate with the help of a catalytic peroxide, and yet the members were apparently told that the oil remained clear. Was it examined microscopically ? It would be a remarkable thing if, under extreme conditions of oxidation, no asphaltic bodies were formed.

The point raised by this introduction was the manner in which the whole scheme of things was working. Is it to be assumed that they got their peroxides and assumed that the peroxides oxidised even the stable oils and, further, apparently produced a certain amount of asphaltic matter which did not do any harm ?

According to Hardy, the presence of 0·7 per cent. of unsaturated acid in lubricating oil was sufficient to cover the surfaces to be lubricated with an adsorptive layer and, although the author was working with 2 gallons in this case, one would think that a few minutes' revolution under the severe oxidising conditions obtaining might produce an amount of acid bodies, or at any rate polar bodies, which was quite adequate for covering the surface. Was it to be understood that this new condition was the result of the adsorption on the surface of some oxidised, or unsaturated, or polar types of bodies ? And was the layer removed so rapidly that one had to keep creating fresh quantities at an enormous rate by this oxidising agency to keep up the necessary supply of unsaturated bodies to keep the surfaces covered ? What he asked for was some exposition giving a picture as to how the thing worked, rather than one which was very eloquent regarding the method of its expression.

Professor J. S. S. Brame said the little picture which Dr. Ormandy wanted might have been furnished perhaps in rather a sketchy outline, if the chemist had taken a hand while the author's investigations had been going on.

Capt. King's paper was extraordinarily valuable, but if the chemist had taken a hand a good deal more would have been learnt.

One of the most striking things, and one which ought to be considered, was the question of the oxidation of the oil from the

point of view of the formation of acidity, because the formation of acid products probably had a great deal to do in explaining the results obtained. One had only to recollect the work of Southcombe and others in connection with oils containing traces of fatty acids to conclude that in all probability acids played a very important part. The paper of Hoblyn's, to which Dr. Ormandy had referred, was published in 1925.[1] Had the visible changes in addition to the chemical changes in the oil been followed up on the lines suggested by Hoblyn a good deal of useful information would have been afforded.

Reference had also been made to the work which Miss Nottage had done.[2] She had investigated the behaviour of a Burmah oil and a Pennsylvanian cylinder oil by extraction with acetone, and had examined the fractions and the original oils by the Hardy method for measuring friction, and some results were not altogether in accord with the author's, because she had found that, with the original oil, for example, as the temperature was increased the coefficient of friction went down until 50° C. was reached, and then the curve changed and there was an increase. An interesting point was that, having extracted from the oils all the "active" constituents, leaving behind the diluent, when that diluent was examined in a Hardy machine, temperature did not affect the coefficient of friction; and neither did the atmosphere, whether oxidation or not.

Personally, he could not but think, when the author referred to his apparatus where 2 gallons of oil were in use, circulated freely and air at 165° C. was blown through the side tube (and it was stated in the paper that the circulation of the oil took place on an average eight times per hour and went on for a long time) that there must have been a very considerable loss by evaporation of the oil. Hoblyn, for example, with his temperature of 250° C., found that in one extreme case the evaporation amounted to as much as 80 per cent. of the oil, and in several cases it amounted to something like 50 per cent. Surely that would account for a tremendous change in the character of the oil, apart altogether from chemical change, and similarly, in the author's experiments, where the oil was sprayed under very drastic conditions in order to oxidise it.

One or two minor points of interest in connection with the paper gave food for thought with regard to some of those newer processes of refining referred to earlier in the discussion—the extraction processes which were becoming so usual now, particularly in America. Were we improving the oils, as lubricants, by doing so?

[1] *J. Inst. Petr. Techn.*, 1925, **11**, 68.
[2] *J. Inst. Petr. Techn.*, 1932, **18**, 943.

We were getting oils which gave better stability tests, it was true. Then, again, there was the question of the behaviour of hydrogenated oils. What was going to be the effect of the oxidation ?

He desired to ask the author if he could give an explanation of the observation that if these oxidised oils were allowed to stand for, in the example given, two months, the oil had undergone such a change as to have but half its oxidation lubrication value. To what was that reversal of action likely to be due ? Personally, he could not understand why an oil which had been oxidised and then kept in air reversed in this remarkable way.

Dr. A. E. Dunstan said it had been his good fortune to have seen much of Mr. King's work during the last two or three years, and to have been immensely interested in this very intricate phenomenon of oiliness or lubricating efficiency. In point of fact, he could go back almost twenty years, because one of the very first papers he had read before the Institution had dealt with that excessively elusive property. What was oiliness ? He had had the chance of seeing Sir William Hardy's work over the last two decades. Hardy had shown definitively that an ordinary so-called stable mass of hydrocarbon oil, on the mere exposure to air, at ordinary atmospheric temperatures, would produce a something, whatever it might be, which conferred the property of reducing the coefficient of friction of that particular material ; and Hardy had shown, equally definitively, that if that particular stuff was exposed to the mere even contact of glass, *e.g.*, by being filtered through beads, then that active body was removed. Moreover, if the same oil, thus deprived of its particularly potent material, were simply allowed to stand exposed to the air, it would in turn be regenerated. Those, to his (Dr. Dunstan's) mind, were extraordinarily amazing reactions of what are ordinarily called stable hydrocarbon oils. It was indeed difficult to realise how these phenomena came about. Take, for example, a material like medicinal paraffin, that represented, say, 40 to 50 per cent. of the original lubricating oil. It had been washed with sulphuric acid, with oleum, and neutralised. It was apparently in an extraordinarily stable molecular condition ; yet, in the twinkling of an eye, this material assumed, for some particular reason, the properties of lubricity. Why was that ? And it could lose these properties equally easily. Were these oxidation problems ? To the organic chemist these phenomena appeared difficult to visualise. He entirely agreed with the author that when one exposed an oil to high temperatures of 160° and 200° C., in the presence of streams of oxygen, it was oxidised ; but how did Capt. King explain that this oxidation occurred at ordinary atmospheric temperatures ? He had

happened that day to have come across an abstract of a paper by Tausz, who said :—

"Along with viscosity, the wetting power or the film-forming capacity of lubricating oils is most important."

Had that point been considered ? What was meant by "film-forming capacity" ? Was it just a measure of the unsaturation of the oils ? Lubricating oils were so thoroughly refined, either by solvents or oleum, by acid and clay, that there were eliminated much of the active and polar molecules. Where was the film-forming capacity coming from ? Tausz went on :—"If the boundary oil layers on metallic surfaces are called into action the result is orientation of the oil molecules." What did that mean ? Tausz talked about the orientation of oil molecules. Why had they orientated ? He further said : "It may be assumed that the adsorbed boundary layers no longer behave as liquids, but as plastic solids." Why ? Were we not getting confused with a mere mass of words ? Such delightful words as "adsorption, boundary layers and plastic layers" were used, but, personally, he would like to know what they meant. Tausz went on : "The aromatic base oils have not got this capacity. They cannot form these boundary layers. The naphthene and the asphalt base oils, and those of vegetable origin, can in all cases form extraordinarily stable and extraordinarily thin layers without rupture. In no case could the aromatic base films be made of a thickness less than 0·5 micro-millimetres. These oils are therefore poor film formers. This supports the idea that the wetting power of lubricants depends not only on the polarity of the molecules, but also on the formation and length of the molecular chain. Lubricating oils of naphthene bases give stronger and more resistant films than those of asphalt bases."

He would like to call upon Capt. King to explain that ! In what did all result ? He had tried years ago to try to get an impression of what function the lubricant fulfilled, and he was more and more convinced that the actual lubricant only applied to the extreme case of boundary friction. What really mattered in this ultimate boundary friction ? To his mind it must be some sort of physical-chemical union—a complex, if one liked, but he was not going to call it physical ; he was going to call it chemical —a chemical complex of the lubricant and the bearing surface. Lubrication was a function of the two things. The lubricant and the bearing surface could not be regarded as independent individuals. There was something which appertained to both. He would like to hear the author's views as to the possibility of his oxidised material, his polar bodies, his reactive stuff forming

some sort of a physical-chemical union with the bearing surface, because, personally, he thought that was the crux of the matter.

Mr. J. Romney said there seemed to be general agreement, based on what all the previous speakers had said, that Capt. King had contributed some very valuable work, but in almost every case he had noticed a general undercurrent which suggested that no real conclusions could yet be drawn. Capt. King's work had been described as "provocative" and as being a "first chapter." On the other hand, Capt. King himself did seem to have drawn conclusions, and what he would like him to do would be to amplify those conclusions. He had told those who were concerned with lubricating oils what he wanted them to produce. Apparently he wanted an oil which would oxidise, and he had come to the conclusion that blends were superior to straight oils. Was that advantage which had been given by the oils which oxidise due entirely to the oxidation products? And if that were the case, would it do, from Capt. King's point of view, to add some of those oxidation products to a stable oil to start with? If the oxidation products had the task only of reducing friction, which result Capt. King had found in his experiments, would any other means of reducing friction do as well? Would Capt. King approve compounding with fatty oil, or the addition of free fatty acid, both of which had the same effect of increasing the original oiliness of the oil? Capt. King was taking a mineral lubricating oil and finding in his test that it took a certain running time to achieve its best lubricating properties, based on the seizing temperature, which figure tended to rise during the test. He also referred to an oxidation lubrication life. Was that life equal to the time taken for the oil to attain its best lubricating power, because if that was the case, was it not rather a pity that an oil could not be started off with that best lubricating power by giving to it that oiliness which it apparently attained after a long period of use?

He would like Capt. King to give his opinion quite definitely on these points. If he might put them again, they were, first of all, would he add oxidation products to start with? Secondly, as he wanted oiliness, would he add anything else which gave oiliness, or did he consider it an advantage to start with an oil which had not the requisite oiliness, but gained that oiliness during use?

As to the oxidation lubrication life, there was one extremely interesting point in the paper. He took it that the lubrication oxidation life could be regarded as the time in this particular test, or in service, taken to reach the point at which the highest seizing temperature was obtained. In Capt. King's experiments with R.N. oil he had carried out an initial oxidation. He had

found that if the oils were oxidised for not much more than 20 hours that oxidation lubrication life had already been exhausted. Yet after 20 hours it could not have been very greatly oxidised, for he said that there were no visible oxidation products. If the useful life of an oil in service could be measured by what Capt. King called the oxidation lubrication life, did he consider that an oil which had been oxidised only to that extent had really finished its useful life ? . If that was the case he would find that there was a large proportion of engines still running on oils which, on that basis, had finished long ago, and which should have been removed, but certainly would not be until their condition was much worse. He would like Capt. King to state definitely whether he considered the oxidation lubrication life was equivalent to the useful life of the oil in the engine, or whether there was justification for its use for a much longer period.

Finally, in considering his results, and especially those concerned with the changes of viscosity during his tests, had Capt. King taken sufficient note of the differences in the initial viscosities of the oils with which he was dealing ? He was dealing with oils which were very widely different in viscosity. When one carried out normal oxidation tests, one would hardly expect as much change in the viscosity of a cylinder stock under a given degree of oxidation as one would of a much lighter straight oil. He mentioned that particularly, because it was pointed out in the paper that the straight cylinder stock which had been used had been subjected to treatment in the apparatus for only 54 hours at under 100° C., and it was mentioned that the coefficient of friction change indicated some increase in viscosity, although at the end of the test the viscosity was the same ; in other words, there had been a reversion of viscosity, which was somewhat difficult to explain. Personally, he would not expect much increase of viscosity under those conditions at all. If that was so, there had been no reversion of viscosity in the original. Had Capt. King any more definite evidence of viscosity change in this case ?

Mr. A. Wolf, in a written contribution, said he would like, first of all, to associate himself with previous speakers who had congratulated Capt. King on his paper and the remarkably fine research work upon which it was based. His own feeling was that the author had been too modest in describing the unique character of the results achieved. When one considered that the lowest coefficient of friction normally obtained in plain journal bearings with " perfectly lubricated surfaces " was of the order of 0·002 (the average value with surface thus lubricated being about 0·006), and that the author and his co-worker, Mr. Jakemen, had succeeded in reducing the coefficient of friction to a figure

which was less than one-fifth the lowest obtained in normal engineering practice, the striking nature of the results became obvious. This was all the more the case when one considered that these results were obtained with one oil, at a temperature as high as 309° C., when the viscosity of the oil would normally be considered quite inadequate to provide "fluid film" lubrication in ordinary hydro-dynamic principles.

He thought he was right in saying that 0·00045 is a lower coefficient of friction than had ever before been achieved in oil-lubricated bearings, not even excepting ball bearings and segmental tilting pad bearings such as those of Kingsbury and Mitchell (the minimum recorded coefficient of friction with these is about 0·0008, and this only at considerably lower speeds and pressure per unit projected area than were used in Capt. King's experiments), and it was very gratifying to think that these results had first been obtained in this country.

Col. Auld had stated, earlier in the discussion, that it was comparatively seldom that temperatures higher than 100° C. were met with in general lubrication practice. He must, however, surely have been referring purely to journal bearings, where, as a matter of fact, the oil-film temperature seldom exceeds about 60–70° C., except in automobile and aero engines operating at high speeds. On the other hand, the temperature of the oil film in the gudgeon or piston pin bearings of internal combustion engines must be considerably over 100° C. even in normal running conditions, and that of the oil film on the cylinder walls higher still.

Another example, of course, was furnished by the lubrication of steam engines operating with highly superheated and/or high pressure steam, where temperatures of 300° C. and over were becoming increasingly common. He agreed, therefore, with Mr. Evans that even the region of highest temperatures, say 250° C.–300° C., explored by Capt. King were by no means lacking in practical importance to the engineer. To the aeronautical engineer they were, of course, of even greater importance, inasmuch as the oil film on the upper portions of the cylinder walls and in the gudgeon pin might easily reach 200° C., and that of the oil in the top piston ring groove over 325° C. These temperatures were, as a matter of fact, often reached in ordinary water-cooled automobile petrol engines when the car was travelling at about 70 m.p.h., even the crank-case oil sometimes reaching a temperature of 130° C., and it was not difficult to see that considerably higher temperatures might be reached in aero engines, particularly the air-cooled radial static type. The aero engine operates at full throttle for most of its running life, and the temperature of the

oil passing from the crank-case to the scavenging pump is frequently 100° C., necessitating the fitting of an oil cooler.

Now, as Mr. Evans had stated, Capt. King, as head of the Air Ministry Engine Research Laboratory at South Kensington, was naturally particularly interested in aero-engine lubrication, and he (Mr. Wolf) gathered that the research Capt. King had described, although also of great general scientific and practical engineering interest, was more particularly directed towards the elucidation of some of the lubrication problems connected with these most highly stressed of all prime movers. Aero engine designers were at present confronted with the difficulty that they were approaching the limit which could be reached in power output for an engine of given weight, not so much on account of lack of strength of the structural materials available, as because even the best lubricating oils at present available were not able to withstand the increasingly severe conditions of load, speed and temperature imposed by raising of the power/weight ratio. Another difficulty was that a large proportion of British aircraft engines, and not a few Continental types, had been designed for use with that exceptionally efficient lubricant castor oil as the chief constituent of the engine oil. There were, however, certain generally recognised objections to the use of either pure castor oil or blends of mineral oil and castor oil rich in the latter constituent. Castor oil was relatively costly, its supply limited by the quantity and quality of the seed harvest, which was apt to be very variable and might fail in times of emergency, and owing to the comparative readiness with which it oxidised when brought into contact with air at cylinder wall temperatures, it was very apt to gum the piston rings, and cause serious lubrication failures unless the piston and rings were very carefully designed and cleaned at frequent intervals. Another important objection to the use of castor oil lubricants, from the Service point of view, was that certain types tend to increase in acidity on storage and also to corrode the ball and roller bearings of engines stored after running on castor base oils and still wet with them, the presence of moisture accentuating this trouble.

Under these conditions it was hardly surprising that attempts should be made either to seek such blends of mineral oil as could be shown to have a lubricating efficiency or " oiliness " approaching that of castor oil, or to treat existing mineral oils in some manner that would raise their " lubricity " to the required standard. It seemed to him (Mr. Wolf) that the author of the paper had already made some very decided advances in that direction. Temporarily, at least, the demands of the aero engine designer would appear to have beaten the oil technologist and it was no exaggeration

to say that the best mineral lubricating oils available to-day had not really sufficient "oiliness" for the more highly-stressed aero engines which had been, as it were, "built round" castor oil.

The remarks of some of the speakers would appear to suggest that they considered that no immediate practical application could be made of the results of the researches described. He was, however, of the contrary opinion, inasmuch as he thought it was by no means unlikely that it might become common practice in the near future to pre-oxidise the lubricating oil intended for automobile and aero engines which are to be used for racing or other special work in which the power unit is stressed to its uttermost capacity. Such activation would probably be too clumsy for ordinary use, as, according to Capt. King's tests, an oil may lose about 50 per cent. of its increased lubricating value if allowed to stand for two months, so that the pre-oxidation treatment should be carried out only shortly before the oil is to be used. However, for racing work, where no trouble within reason was too great in order to obtain the utmost power output from the engines, the procedure suggested would certainly not be considered unduly cumbersome. Certainly the selling of super-efficient racing oils on the principle of being "warm from the cow" would strike a decidedly novel note, not unreminiscent of a famous brand of crustless cheese long sold in small packages each bearing on the wrapper a certificate stating up till what date the beneficent bacilli contained therein might be expected to retain their maximum activity.

Further research would no doubt be prosecuted in the near future to see whether it would not be possible to activate oils in such a manner that they retained their increased lubrication efficiency for much longer periods, and it was possible that the transference of the oil to a hermetically sealed container immediately after activation might be found a partial solution of the problem, although, in addition, it might be found necessary to displace the air in the free space above the container with some inert gas such as nitrogen.

It was obviously impossible to answer difficult questions as to what was the cause or what were the causes of the increase in lubrication activity until both the used and unused oils had been subjected to exhaustive chemical analysis, but he thought most oil chemists would suggest right away that the formation of "petroleum acids" would be one of the most obvious. It was, of course, well known that many mineral oils showed a marked increase in acidity when oxidised, and at the same time the important researches of Southcombe and Wells had shown that the addition of as little as 0·6 per cent. of a fatty acid to a

mineral lubricating oil reduced the coefficient of both static and kinetic friction to a marked degree, due, presumably, to the formation of an "adsorbed film" of fatty acid on metallic rubbing surfaces with which the oil comes into contact. It was not unreasonable to suppose that some at least of the organic acids formed by the oxidation of mineral oils were at least as potent as the higher fatty acids in this respect and might, under certain conditions, be even more so. As long ago as 1923 the writer, in conjunction with Mr. Gooday, carried out some researches on these lines, a medium, heavy viscosity, high-grade internal combustion engine, straight mineral lubricating oil being oxidised by passing through it a current of air containing 600 parts per million of ozone at a temperature of 110° C. After 24 hours of this treatment the oil contained 2·4 per cent. of petroleum acids, and after a further 40 hours' oxidation the acid content had risen to 4 per cent. Samples of the oil drawn off at these two stages of oxidation were subjected to mechanical friction tests (he thought in a Deeley machine at the National Physical Laboratory) and gave coefficients of friction very decidedly below those of the original oil. The tests were not, however, anything like as exhaustive or severe as those carried out by Capt. King and Mr. Jakemen. As far as they went, they agreed with the results obtained by those two workers and also with the very interesting results quoted by Dr. Redgrove for oils after exposure to the Air Ministry oxidation test. There was one other example of what might be "oxidation lubrication" which was of interest because it was frequently met with in actual practice, and that was the formation of "oil varnish films" on the rubbing surfaces of Michell bearings. Mr. J. Foster Petree referred to these in the following terms during a discussion following a paper on lubrication read by Mr. S. E. Bowrey before the Institute of Marine Engineers in March, 1926: "It is a common experience with Michell bearings that a kind of oil varnish is formed on the bearing surfaces after prolonged periods of running under load. Sometimes, when an overhaul has been in progress, a zealous fitter has carefully scraped this off, but it is found to be the reverse of beneficial to do so. Present practice is to leave this "skin" in place. . . . It appears to be pressed into the metal, and seems distinctly conducive to frictionless running." In his reply Mr. Bowrey stated that the oil varnish described by Mr. Petree was probably formed by oxidation of the oil. He (Mr. Wolf) was not suggesting that the films formed on the rubbing surfaces in Capt. King's experiments were visible to the eye like those formed on Michell bearings, but there might be a distinct parallelism between the two series of phenomena.

It was obvious that at the higher temperatures in Capt. King's experiments, in the case of, for example, the M.B. oil, as Dr. Ormandy had remarked, a good deal more than mere oxidation in the sense of direct chemical combination with atmospheric oxygen was going on, the most pronounced reaction over the temperature range 250° C.–310° C. being probably "condensation," *i.e.*, the combination of atmospheric oxygen with the one hydrogen atom from each of two adjacent oil molecules, with formation of steam and simultaneous linking up of the oil molecules to form larger molecules. This reaction, which closely resembles polymerisation, might be repeated until the size and carbon-hydrogen ratio of the molecular aggregates thus formed became sufficiently high to convert them into "blown" or "oxidised" asphalt. Hundreds of tons of "blown" asphalt for the bituminous felt industry, etc., were, of course, manufactured every day by this well-known process, and it was obvious that if too much asphalt was formed during the oxidation of an internal combustion engine oil in service any advantage gained by the increase in the "oiliness" of the oil might be more than outweighed by the loss in power resulting from the formation of asphaltic and carbon deposits on the piston walls, etc.

Capt. King had, as a matter of fact, already realised this, and in the August 25th, 1933, number of Engineering published a paper giving a very interesting account of some researches on the lubrication of petrol engines with mineral oils to which a small proportion of lead tetra ethyl had been added for the purpose of reducing its tendency to oxidise in service. The beneficial effect of the lead "dope" was very marked, the rate of formation of oxidation asphalt on the piston walls being very much reduced, and consequently the power output of the engine increased owing to reduction of piston drag. It would at first sight appear that the chemical stability of oils towards oxidation would be incompatible with capacity for receiving improved "oiliness" by oxidation, but this might not necessarily be the case, for whereas the intensive refining of an oil with concentrated sulphuric acid and/or decolourising clay might reduce its tendency to form asphaltic sludge on oxidation, it did not necessarily reduce its tendency to react with atmospheric oxygen with formation of organic acids at higher temperatures, and any increase in "oiliness" might be due to the latter type of oxidation alone. Similarly, the addition of metallic "dopes" to lubricating oils need not necessarily check what one might call "beneficial" oxidation.

He was very glad to note that the author of the paper adopted circulation oiling for his test bearings. Mechanical tests on

lubricating oils had, in the past, been far too much restricted to the "all loss" method of feeding the bearing in which only fresh oil was supplied. Practical engineers were more interested in the behaviour of oil which had already been in use, as most journal bearings in which high-grade oils are used are fed from a circulatory system.

In conclusion he would like to ask the author if he had obtained comparable results with compounded oils and also with castor oil, and whether he had carried out any experiments with bearing surfaces prepared by lapping, grinding and polishing after trueing up in a lathe, the use of doped castor being omitted.

Prof. A. W. Nash wrote: Capt. R. O. King's experiments give confirmation to the well-known fact that the polar bodies formed when hydrocarbon lubricating oils become slightly oxidised, as often occurs in practice, increase the lubricating properties of such oils. Friction machine experiments using loaded oxidised oil films have been already described by Dover and Appleby[3] and Nash, Stanley and Bowen,[4] and a beneficial effect noted in the case of oxidation of mineral oils.

The question which arises from our existing knowledge is: should this uncontrolled oxidation action described by Capt. King be used to supply the property necessary for some lubricants or should not lubricants for special higher temperature conditions be oils of high resistance to oxidation in which suitable polar bodies have been incorporated.

Capt. R. O. King, before replying to the discussion, said that the friendly and constructive nature of the criticism offered was most encouraging, and an ample reward for the effort required to prepare the paper presented.

Replying to the Chairman, Mr. J. McConnell Sanders, the formation of boundary layers was considered to be due to the presence in the oil of particularly active (polar) molecules, capable of adhering strong to surfaces. The experiments described were taken to show that such molecules were formed in mineral oils by oxidation processes. The effect of sulphur compounds was of particular interest at present in view of the experiments being done in America on high pressure lubricants, but the action of these compounds had not yet been investigated. It was agreed that determinations of the chemical and physical properties of the various oils used, during the course of the lubrication trials, would have been of great interest. The evidence that oxidation *products* were formed was entirely visual. The colour changes

[3] *Ind. Eng. Chem.*, 1926, **18**, 63.
[4] *J. Inst. Petr. Techn.*, 1930, **16**, 853.

mentioned applied particularly to oil R.N. and no doubt indicated an oxidation change of some sort, although it was not accompanied by the deposition of sludge even after very long standing. The colour changes were not necessarily due to finely-divided metals or to the products of combustion arising from the gas burner, as suggested, because they were most pronounced when the oil was oxidised before use in the testing machine and in the absence of the factors mentioned. The question as to the advisability of renewing the oil in an engine sump was of considerable interest. The oil in the sump of an ordinary motor car is generally renewed frequently on account of the usual unnecessarily high rate of oil consumption. The oil remaining in the sump tends to be loaded with undesirable constituents, and in many cases the oxidation activity necessary to improve the lubricating value would not occur in the crank-case but only after the oil had passed into the space between the piston and the cylinder. It is not " used " oil which is a good lubricant, but oil in a certain state of oxidation activity. It is not recommended, therefore, that motorists should cease to either clean out their crank-cases or to filter the oil being used.

The remarks of Col. Auld were particularly gratifying because it was not until after the experiments had been completed and the results considered that it was learned that the characteristics of the several oils, as shown by the experiments, were those known in practice. One of the objects of the paper was to give a rational explanation of why blends having similar physical properties differed in lubricating value, and it followed, as Col. Auld suggested, that the usual " specification " did not cover lubricating value or even the durability or life of an oil. A knowledge of the behaviour of oils at the very high temperatures of the experiments was of particular interest in respect of piston lubrication, especially pistons of air-cooled engines. The viscosity of oils at such high temperatures approaches that of water, and the value of an oil as a lubricant must depend on some other property, because a fluid film capable of carrying a load cannot be formed in the conditions of use.

The observation of Mr. Barton that the results of oxidation lubrication, which depend on the formation of a strongly adherent film, are somewhat similar to those obtained with extreme pressure lubricants, is of interest. The consequent suggestion that experiments should be made with variable loads has been anticipated to some extent by Mr. Jakeman, and it is hoped that the interesting results obtained will be available for publication in due course. Mr. Barton's question as to the effect of oxidation lubrication in an engine raises an extremely interesting point, which has been dealt

with in a preliminary way in a recent publication.[5] Thus, the primary effect of oxidation on piston lubrication is to diminish friction, but in the circumstances the products of oxidation can accumulate in piston ring grooves and on the piston surface, leading to an increase of friction much greater than the decrease due to oxidation activity.

It is gratifying that the experimental results described by Dr. Redgrove are in agreement with those obtained with so dissimilar an apparatus as a journal bearing. The same observation applies to some of the experimental results described by Hardy and Nottage as mentioned in the paper. It is to be remembered, however, that friction measured by the Hardy type of apparatus, using a spherical slider, is taken to be that on the adsorbed layer and that if the loading and other conditions led to the corresponding type of friction in a journal bearing, seizure would occur immediately. The point is that some care must be taken when comparing adsorbed layer friction with that prevailing on the surface of a film perhaps 100 times as thick.

The problem of "running in" mentioned by Mr. Evans is not in a state of finality. The running in of white metal bearings is probably due to "flowing" of the metal under the influence of temperature and pressure. The condition of the bearing improves with use and accounts for the term "anti-friction metal." A bronze bush running on a steel journal does not seem to improve appreciably with use, and the friction observed during trials in conditions when fluid friction ceases to be the controlling factor depends on the nature of the *initial* surface finish. Prior to the trials made using mineral oils to lubricate a bronze bush run in on doped castor oil, it was found[6] that the combination of vegetable oils with lead dope was of especial interest. Thus castor oil added to engine fuel containing 12 ml. of ethyl fluid per gallon had no measurable effect to reduce the detonation delaying effect of the dope, whereas other oils, especially oleine, acted deleteriously on the beneficial effect of the dope. On the other hand, the effect of iron carbonyl as a fuel dope was almost completely destroyed by the small addition to the fuel of 1 per cent. of castor oil or of oleine. There may appear to be some connection between these effects and the running in effect of doped castor oil, but that has not been established. The engine experiments indicate, however, that the decomposition of the lead dope to the detonation delaying oxide is not prevented by the presence of castor oil, so in the journal bearing lead oxide may be obtained and act either as a finishing substance or as a filling material. The second query of Mr. Evans really deals with

[5] King, *Engineering*, August 25, 1933.
[6] King and Moss, *Engineering*, July 11 and 25, 1930.

the primary and secondary friction effects described in reply to Mr. Barton. The answer is that if an oil is used in circumstances where the accumulation of oxidation products leads to a large secondary friction effect, it may be on the whole an advantage to control oxidation to prevent the formation of partial products even if lubricating value is diminished.

Some leading questions, very difficult to answer, are put by Dr. Ormandy. There seems to be some slight confusion about the premises on which the questions are based. The oil which remained clear during use was R.N., and it showed no improvement in oxidation lubrication value when run at the high temperatures made possible by improving the surface of the bush. The greatest improvement during use was observed for oil M.B., in which visible oxidation products accumulated to a notable extent. The R.N. oil is a single variety and the M.B. a blend in which peroxidation would be more likely to occur. It is considered that oxidation lubrication is maintained by the formation of active molecules, which build up to a layer of appreciable thickness. The layer must have rigidity in a direction normal to the surface in order to carry the load, but the surface must be able to shear off in the direction of motion with little resistance in order to account for the friction becoming so low that the co-efficient may be less than 0·0005. A continuous supply of activated molecules is therefore required, and is more likely to be obtained at a sufficient rate over a long period in blends containing one constituent such as cylinder stock, in which oxidation is promoted by the active oxidation products formed more readily in another and less resistant constituent.

The lack of chemical supervision of the experiments is mentioned by Professor Brame, and it is agreed that a great deal of useful information was thereby not obtained. The explanation is that the experimental work developed in unexpected directions not fully appreciated until it was nearly finished. Acid values were, however, determined during some of the early trials, due to the suspicion that a reputed mineral blend contained a small proportion of oleic acid. The acid value of a blend known to be entirely mineral was found to develop during the trials to an extent corresponding with the addition to the fresh oil of from 1 per cent. to 2 per cent. of oleic acid. As to the loss by evaporation during the trials, this again was not measured accurately, but was never excessive. The temperature of the oil in the sump was about 70° C. to 80° C. and the rate at which air at 160° C. blown into the closed circuit was not sufficient to raise the temperature of the oil stream as a whole, more than 10° to 15° C. The loss from evaporation occurred mainly from the oil emerging from the hot loaded

surfaces, which were raised to temperatures exceeding 200° C. for daily short periods only. The explanation requested by Professor Brame for diminution of oxidation lubrication value of an oil on standing seems to lie in the difference between an oxidised oil and one in a state of oxidation activity. Oxidation activity requires the two factors of air and elevated temperature and dies down when the stimulation due to the last mentioned factor is removed.

The feature of Hardy's work mentioned by Dr. Dunstan needs no comment other than made in the introductory part of the paper, except to mention the difficulty of attributing changes of lubricating value at room temperature, to oxidation. It must be remembered, however, that the change improving lubricating value occurred after the oil had stood in contact with air, but not after similar exposure to nitrogen. Again, Hardy's method measures the friction on the adsorbed layer, which is supposed not to exceed one or two molecules in thickness, and the formation of an extremely minute proportion of polar molecules in the surface exposed to air would suffice to alter the nature of the adsorbed layer formed when the oil was applied to the surface to be lubricated. Dr. Dunstan discusses the interpretation of the experimental work of Tausz, but comment on it at this time would be too much in the nature of pure speculation. Dr. Dunstan discusses also what Hardy calls "The problem of the boundary state," but the object of the paper presented is mainly to show that the type of friction obtained in the experiments described prevails on the surface of a built up boundary layer. The term boundary friction has been applied loosely in the past, and it is suggested that the adsorbed layer, which is so closely united with the metal surface that it cannot be removed without abrasion, should be regarded as the true boundary, thus allowing for a boundary *layer* decreasing in rigidity with thickness, to build up on it. We are concerned to-night with the properties of the surface of the built up boundary layer.

The information asked for Mr. Romney cannot all be supplied. Oxidation products should not be added to oil, because it is the activity producing them that is wanted, not the resultant products. An addition of fatty oil or free fatty acid would be made if the oil were to be used in circumstances preventing the formation of an unbroken fluid film, and further, if the increase of decomposition products to be expected would not be objectionable. Oxidation lubricating life is the period over which corresponding activity is maintained ; for example, oil M.B. ran for 100 hours after attaining maximum lubricating value before showing any sign of distress. The time required to attain maximum oxidation lubricating value during the journal bearing trials was excessive ; it could no doubt be shortened. The engine trials mentioned earlier show that a

suitable blend of mineral oils attains oxidation lubricating value while passing the piston. When the oxidation lubrication life is exhausted the oil is still a viscous fluid and may be used as such, but seizure might occur immediately on a rupture of the film, or if load were insufficient to cause actual seizure, excessive wear would be expected. These views are supported by measurements of wear made during the lubrication trials described in the paper. The trials made with cylinder stock were as Mr. Romney mentions, carried on for a relatively short time. This was because the general procedure was based on continuing a trial only so long as measurable changes of μ min. and seizing temperature were observed. The M.B. oil trial was continued for a very long period, because the seizing temperature had gone beyond the limit observable, and an unexpectedly long running period elapsed before it "came back on the scale." The variations of viscosity of oil C.S. were judged by the value of $\mu 40°$ and present some anomalies which are difficult to explain.

Several of the points covered by Mr. Wolf's written contribution have been dealt with. When discussing coefficients of friction one should keep in mind the early experiments of Professor Kingsbury,[7] made with very carefully finished bronze bushes. Consideration of these experiments would have shown many subsequent workers that their relatively high measured coefficients of supposed *fluid friction* were in fact coefficients of mixed types of friction, and therefore of little significance. The effects of oxidation in practice, described by Mr. Wolf, are of interest, especially that relating to the film formed on Michell bearings. It is regretted that information has not been obtained on the effect of oxidation activity on compounded oils. Some trials were made using castor oil, but were mainly for the purpose of determining the effect of metallic dope. The effect of bearing surfaces carefully finished mechanically was observed. The experiments have been described briefly in a previous publication.[8]

Prof. Nash, in his written contribution, sets a question which cannot be answered satisfactorily until further experiments have been made. The question does, in fact, cover the present line of endeavour if it be qualified by including the temperature and other conditions in which the rationally compounded or blended oils are to be used.

[7] *Amer. Soc. Mechl. Eng.*, p. 143, 1903.
[8] *Proc. Roy. Soc. A.*, Vol. 139, 1933.

The Rôle of the Time Factor in the Acid Treatment of Cracked Distillates.*

By F. Sager, D.Sc. (Assoc. Member).

The chief factors governing the reactions taking place in the acid treatment of cracked distillates are :—

(*a*) Concentration of acid employed.
(*b*) Amount of acid.
(*c*) Temperature at which treatment is carried out.
(*d*) Time of contact between acid and oil.

While the first two factors have been studied in an exhaustive way,[1] and there are very valuable contributions on the influence the temperature has on the results of refining,[2] the time factor has received comparatively less attention and there are only few data to be found in the literature.

In the "Scientific Principles of Petroleum Technology" (Gurwitch and Moore, 1932), it is stated that the quality of the refined petroleum products may suffer as the result of too short, as well as too long, duration of the action of the sulphuric acid. In general, for laboratory purposes, five to ten minutes, corresponding to half-hour to one hour in large scale working, are considered to be sufficient.

Brooks, in his classical work on the action of sulphuric acid on petroleum distillates,[3] shows that the yield of polymers increases with the time. An example is cited for the formation of polymers from secondary octyl alcohol between a time limit from 15 to 135 minutes.

Rue and Espach[4] state that the quality of the treated product may be effected by the length of exposure to the action of the acid and that there is a tendency in the industry to reduce this contact time.

Zublin[5] improved the colour of a gasoline of 88 octane number, by reducing the contact time to 60 seconds and thus losing only 2 octane numbers, with a polymerisation loss not higher than 2 per cent.

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* Paper received November 28, 1933.

[1] Brooks and Humphry, *J.A.C.S.*, 1918, **40**, 822; Egloff, Levinson and Herrmann, *J. Inst. Petr. Techn.*, 1932, **18**, 282; Morrell and Egloff, *World Petroleum Congress*, 1933, **2**, 10; Morrell, *Nat. Petr. News*, Dec. 17, 1930; Jan. 21, 1931; Bespalow, *Chem. Abs.*, 1930, **24**, 1731; Born, W., *Petr. Ref. Assoc.*, April 5–6, 1933; Wirth, Kanhofer and Murphy, *Oil & Gas J.*, July 31, 1933; Manning, *World Petroleum Congress*, 1933, **2**, 7.

[2] Klemgard, *Ref.*, 1927, **6** (5), 51; Halloran, *Oil Bull.*, 1928, **14** (1), 88.

[3] Brooks and Humphry, *J.A.C.S.*, 1918, **40**, 822.

[4] Rue and Espach, *U.S. Bur. Mines Bull.*, 333, 1930.

[5] Zublin, *Proc. A.P.I.*, Dec., 1932, Sect. III., p. 79.

Trival[6] describes a treating plant of 10,000 barrel daily capacity in France, using De Laval separators as means to keep the contact time limited to a few seconds.

Trusty[7] mentions the influence of the time factor on the sulphur, colour and acids formed during re-running.

Born,[1] in his work on the influence of the amount and concentration of acid on the loss on octane numbers, finds some influence of the mixing and settling time on the quality of the finished product. Under the conditions of his experiments he has chosen five minutes mixing and one hour settling.

The purpose of the work reported here was to add some information on the subject by investigating the influence of the time factor on the results of acid treatment of some representative cracked distillates as obtained from different crudes in different type cracking plants.

Tables A. and B. show the results on a pressure distillate obtained by cracking Rumanian semi-paraffinous Pacura (Mazut) in a Dubbs cracking plant by the non-residue method.

In this and in the following cases the refining technique was chosen as simple as possible, as the prime purpose was not to make the best possible finished gasoline, but to get the maximum of information on the effect of the acid treatment as such.

The temperature at which the acid treatment was carried out varied with the room temperature around 20° C.

No wash of any kind was given before the acid treatment.

After the acid treatment the product was water and soda washed (except in case of Tables C. and D.), then redistilled. No wash was applied after redistilling.

The apparatus used for the acid treatment consisted in a turbo mixer which was tried at different speeds (1200 to 2200 r.p.m.). The contact time given in the tables is also the actual mixing time, except the case where gravity settling was employed. A De Laval S-N acid sludge separator was used to effect the instantaneous separation of oil and acid.

The determination of the yield of a fraction of a given final boiling point was carried out by distillation under direct fire, using a Hempel column for fractionation. The yield was determined by weight, then calculated by volume, and a distillation carried out by heating the pressure distillate on an oil bath to 150° C., and introducing direct steam under standardized conditions, until the calculated volume had distilled over. On the product thus obtained the tests and the chemical analyses were

[6] Trival, *Ref.*, 1932, **11**, 313.
[7] Trusty, *Ref.*, 1932, **11**, 455.

carried out. The description of the methods used is given in the annex.

The examples given in the tables, in each case, are, first, the raw distillate; second, the product treated with the shortest contact time which would give a gum figure, and a stability at least as good as for a product obtained by 20 min. mixing and 1 hr. settling. It may be said here that efficient mixing proved 5, 10 and 20 min. gave no differences, except those which are within the experimental error. As example for the gravity settled product, 20 min. mixing and 60 min. settling were chosen, because this represents in practice often the actual treating time.

TABLE A.

Rumanian Dubbs Pressure Distillate Treated with 3 per cent. by weight Sulphuric Acid (98 per cent. H_2SO_4).

	I. (raw)	II.	III.	IV.
Time of contact with acid	0	6 sec.	15 sec.	80 min. (20 min. mixing—60 min. settling)
Specific gravity	0·806	0·806	0·806	0·809
Acidity (mg. KOH)	0	0·2	0·2	0·56
F.B.P. (A.S.T.M.)	264° C.	264° C.	269° C.	281° C.
Di-alkyl sulphates (gr. H_2SO_4/100 gr.)	—	0·083	0·088	0·122

TABLE B.

200° C. F.B.P. Fraction Prepared from Pressure Distillates—Table A.

	I.	II.	III.	IV.
Yield by weight	60·5%	60·0%	58·0%	55·0%
Specific gravity	0·759	0·756	0·756	0·755
Gums (copper dish)	220 mg.	21 mg.	13 mg.	37·7 mg.
Doctor test	positive	negative	negative	negative
Sulphur	0·048%	0·035%	0·035%	0·032%
Octane number (S-30 eng., 212° F. jacket temp., 22° spark advance)	64	63	62	61
Chemical composition :—				
Diolefins	1%	—	—	—
Olefins (diolefins included)	48%	43%	40%	32%
Aromatic hydrocarb.	2%	2%	2%	2·6%
Naphthenic hydrocarb.	30%	33%	35%	38·4%
Paraffin hydrocarb.	20%	22%	23%	27%

TABLE C.

Russian Dubbs Cracked Pressure Distillate, Treated with 0·7 per cent. by Weight of Sulphuric Acid (96 per cent. H_2SO_4).

	I. (raw)	II.	III.
Time of contact with acid	0	25 sec.	80 min. —20 min. mixing. —60 min. settling.
Specific gravity	0·786	0·787	0·789
Acidity (mg. KOH)	0	0·22	0·33
Di-alkyl sulphates (gr. H_2SO_4/100 gr.)	0	less than 0·01	0·01

Tables C and D give another example of Dubbs cracked gasoline. The cracking stock was a semi-paraffinous Russian Mazut, the type operation Flashing. In this particular case the acid-treated pressure distillate was not neutralised with soda but with a soda plumbite solution.

TABLE D.

185° C. F.B.P. Fraction from Distillates—Table C.

	I.	II.	III.
Yield by weight	52·8%	52·2%	51·0%
Specific gravity	0·744	0·743	0·742
Gums (copper dish)	190 mg.	26 mg.	28 mg.
Doctor test	positive	negative	negative
Sulphur	0·035%	0·016%	0·016%
Octane number (S-30 engine, 212° F. jacket temp., 22° spark advance)	76·8	75·0	73·5
Chemical composition :—			
Diolefins	0·8%	—	—
Olefin hydrocarbons (including diolefins)	42·0%	40·5%	36·0%
Aromatic hydrocarb.	5·0%	5·0%	5·5%
Naphthenic hydrocarb.	35·5%	36·5	39·0%
Paraffin hydrocarb.	17·5%	18·0%	19·5%

Tables E and F show the influence of the time factor on the acid treatment of an end point distillate obtained by cracking Texas fuel oil in a Cross cracking plant.

TABLE E.

Texas End-point Distillate from a Cross Plant Treated with 1·5 per cent. Sulphuric Acid (78 per cent. H_2SO_4).

	I. (raw)	II.	III.
Time of contact with acid	0	15 sec.	80 min. —20 min. mixing. —60 min. settling.
Specific gravity	0·735	0·736	0·739
Acidity (mg. KOH)	0·025	0·025	0·1
F.B.P. (A.S.T.M.)	185° C.	189° C.	194° C.
Di-alkylesters (gr. H_2SO_4/100 gr. oil)	0	0·005	0·01
Gums (copper dish)	140 mg.	81 mg.	133 mg.

TABLE F.

180° C. F.B.P. Distillate Prepared from Distillates—Table E.

	I.	II.	III.
Yield by weight	94%	93·5%	92%
Specific gravity	0·733	0·733	0·732
Gums (copper dish)	100 mg.	27 mg.	30 mg.
Doctor test	negative	negative	negative
Sulphur	0·02%	0·015%	0·011%
Octane number (S-30 engine, 212° F. jacket temp., 22° spark advance)	64·6	63·6	63·2
Chemical composition :—			
Diolefins	traces	—	—
Olefins (including diolefins)	21·5%	20·5%	16·5%
Armomatic hydrocarbons	8·5%	8·5%	9·0%
Naphthenic hydrocarbons	29·6%	30·5%	31·5%
Paraffinic hydrocarbons	40·4%	40·5%	43·0%

Finally, Tables G H and J show some of the results obtained with the heavy fraction of a cracked distillate. Cracking stock in this case was Venezuela gas oil, the cracking plant a tube and tank unit. For the determination of gums and octane numbers, the heavy fraction, after redistillation, was blended with a light fraction in the proportion 1 : 1. The light fraction had a sp. gr. of 719, 50 per cent. boiling over at 100° C., 75 per cent. at 175° C., F.B.P. 202° C.

TABLE G.

Heavy Cracked Distillate from Venezuela Gas Oil (Tube and Tank Plant) Treated with 2 per cent. Sulphuric Acid (98 per cent. H_2SO_4).

	I.	II.	III.	
Time of contact with acid	(raw) 0	7 sec.	80 min.	—20 min. mixing. —60 min. settling.
Specific gravity	0·786	0·786	0·789	
Acidity (mg. KOH)	0·19	0·31	0·51	
A.S.T.M. distillation :—				
—100° C.	2·5%	2·5%	2·0%	
—200° C.	95·0%	94·0%	91·0%	
F.B.P.	210° C.	212.5° C.	236·5° C.	
Di-alkylsulphates (gr. H_2SO_4/100 gr. oil)	—	—	traces	

TABLE H.

205° C. F.B.P. Distillate Prepared from Distillates—Table G.

	I.	II.	III.
Yield (by weight)	95·6%	94·5%	91·0%
Specific gravity	0·786	0·786	0·785
Doctor test	positive	negative	negative
Sulphur	0·071%	0·036%	0·028%
Chemical composition :—			
Diolefins	traces	0	0
Olefins	31·5%	15·0%	25·0%
Aromatic hydrocarbons	19·5%	23·0%	21·5%
Naphthenic hydrocarbons	26·0%	30·0%	27·5%
Paraffinic hydrocarbons	23·0%	32·0%	26·0%

TABLE J.

Distillates—Table H—Blended with Light Gasoline (1 : 1).

Gums (copper dish)	119·8	23	23
Octane number (S-30 engine, 212° F. jacket temp., 22° spark advance)	68·4	68·0	67·7

It has been found that for the elimination of the diolefins and the most unstable olefines, 5 to 25 secs. were enough if sufficiently intimate contact was provided. The amount of acid used had a certain influence on this time ; with more acid the contact time could be kept on the lower side, the inverse being true for small amounts of acid. As the formation of gums is chiefly a catalytical reaction, it is, of course, necessary to have every trace of the diolefines removed. The amount of acid used and the violence of mixing have a similar effect in this respect.

The speed of polymerisation of the olefines is high up to about

80 secs., from when on it slows down considerably, to be hardly detectable from 100 secs. on. This observation, which follows from the chemical composition of the cracked distillates at the various stages of the process, is in a sensitive way checked by the determination of the decrease in knock-rating and the increase in final boiling point. These phenomena are directly related to the polymerisation losses occurring during the acid refining or, in other words, to the yield of finished gasoline, obtainable from a given raw cracked distillate. For the distillates investigated, the polymerisation losses are between 5·5 and 1·8 per cent. for long contacting and 1·1 to 0·6 for short contacting.

The effect on the aromatic hydrocarbons was within the experimental error, and it can be deduced that their total percentage in the finished gasoline changes relative to the olefines eliminated.

The naphthene and paraffin hydrocarbons were unattacked.

The sulphur content, also not very high in the raw materials investigated, shows to be considerably lowered in any of the treated gasolines.* This is, of course, to some extent due to the washing taking place after the acid treatment, and does not purely represent the effect of the sulphuric acid. A determination of the total sulphur in the acid gasoline, before washing it, does not convey any information as to what has happened to the original sulphur because of the secondary reactions which have taken place between acid and oil.

The formation of the oil soluble di-alkyl-sulphates, which cannot be removed by water or soda wash, and which easily decompose during redistillation, thus badly affecting the stability and causing increased gum[8] are refrained to a certain degree by short contact time.

The lower acidity in the case of short contacting indicates also reduced formation of the water soluble mono-alkyl-sulphates.

Appendix.—Methods of test and chemical analyses referred to in this paper.

Standardized or commonly used tests are indicated as such in the tables and need no further reference or description here.

The acidities given in the tables for the treated cracked distillates are determined immediately after the indicated settling time.

The method for the determination of the four principal hydrocarbon groups is the one given by Egloff and Morrell.[9]

The sulphur was determined by the lamp method A.S.T.M.

* Since this paper was finished, experiments have been carried out with a cracked gasoline from Iraq crude. By using the same amount of acid, the original sulphur content of 0·37 per cent. has been reduced to 0·12 per cent. in the case of 10 secs. contact with acid, and to 0·11 per cent. by 75 mins. contact.

[8] Moser, *Petr. Z.*, 1932, **26**, 4–6.

[9] Egloff and Morrell, *Ind. Eng. Chem.*, 1926, **18**, 354.

D. 90–26 T. The sulphuric acid liberated by the di-alkyl-sulphates, present in the acid-treated cracked distillate, after the conventional water and soda wash and before redistillation, has been determined by saponification with alcoholic soda solution. 50 gr. (or 100 gr.) of oil, 10 ml. n/2 alcoholic NaOH and 10 ml. of benzole were heated on the water-bath under reflux cooler for half-hour, then cooled and the remaining free NaOH titrated back with n/2 sulphuric acid. A parallel test without oil was carried out to determine the necessary correction on the result obtained.

The estimation of diolefins was carried out by heating 250 ml. of oil with 5 gr. maleic anhydride on the water-bath, under reflux cooler, for 1 hr. After cooling, the gasoline was decanted from the newly formed crystals of acid anhydrides, the unchanged crystals of maleic anhydride and the heavy viscous oil formed in some cases. Then the gasoline was water and soda washed and redistilled to its original final boiling point. A parallel test without the addition of maleic anhydride was carried out, and the losses found deducted from the losses of the maleic acid treatment, the difference being the diolefins.

The action of the maleic anhydride on hydrocarbons with conjugated double bonds has been thoroughly investigated by Diels and Alder.[10] Birch and Scott[11] have used this reaction for the identification of diolefins in vapour-phase cracked gasoline, and consider that the quantitative determination of diolefines appears to be possible for the cyclic hydrocarbons, but that the reaction is rather slow for the straight chain diolefins. I. G. Farbenindustrie A.-G. has taken out British Patent 352,164 (July 9, 1931) for the purification of crude benzole by means of refluxing it with 0·3–10 per cent. maleic anhydride for 2 hrs. and then redistilling it.

As it was within the purpose of the work described in this paper to study the time action of the acid refining on the most reactive group of the unsaturated hydrocarbons, chiefly responsible for excessive gum formation and unstability, the method in the form as described above, was found very valuable as a criterium for the minimum length of time, which has to be adopted in contacting oil and acid.

Untreated or undertreated gasolines showed the peroxide reaction with vanadic acid[12] immediately after redistillation, while gasolines, which were refined to a point where they no longer reacted with maleic anhydride, showed the first indication of peroxide formation not before 10 days.

[10] Diels and Alder, *Ann.*, 1928, **460**, 98; *Ber.*, 1929, **62**, 554; *Ann.*, 1929 **470**, 62; *Ber.*, 1929, **62**, 2081.
[11] Birch and Scott, *Ind. Eng. Chem.*, 1932, **24**, 29.
[12] Jorissen, *J. de Pharm. de Liège*, 10, No. 2.

The Calculation of the Mean Temperature Difference in Multi-Pass Heat Exchangers.*

By A. J. V. Underwood, D.Sc., M.I.Chem.E.

In single-pass heat exchangers, for parallel flow or counter-current flow, the mean temperature difference is given by the logarithmic mean. The derivation of this formula depends on the assumptions that :—

(1) The coefficient of heat transfer does not vary.

(2) The specific heat of each fluid remains constant.

(3) The mixing of each fluid is sufficient to ensure that its temperature is uniform over any cross-section.

With these same assumptions, the mean temperature difference in multi-pass heat exchangers is not given by a logarithmic mean formula. Nagle[1] has pointed out that serious errors may arise if the logarithmic mean formula is used for multi-pass exchangers, and has derived a series of curves giving correction factors to be applied to the logarithmic mean temperature difference to give the actual mean temperature difference. These curves are obtained by trial and error solution of the differential equations for heat transfer. It will, however, be shown that it is possible to obtain a solution of these equations whereby the mean temperature difference is expressed in terms of the inlet and outlet temperatures of the two fluids. As pointed out above, the assumption is made that the mixing of the fluid on the shell-side is sufficient to ensure uniformity of temperature over any cross-section of its flow. The use of baffles in such heat exchangers renders this assumption one that is reasonably in accord with practical conditions. It is further assumed that the heating surface is the same in each pass.

Where the assumption that the specific heat of each fluid is constant is not fulfilled and an appreciable variation occurs through the exchanger, as may be the case with petroleum fractions, allowance may be made in the formulæ derived below by taking as the specific heat of each fluid the arithmetic mean of its specific heats at its inlet and outlet temperatures. Where the specific heat is a linear function of the temperature, this is of course equivalent to taking the specific heat at the arithmetic mean of the inlet and outlet temperatures. Similarly, when the heat transfer coefficient varies with the temperature a mean value for the exchanger would be taken.

* Paper received September 11, 1933.

[1] *Nagle, Industrial & Engineering Chemistry*, 1933, **25**, 604.

One Pass on the Shell Side, Two Passes on the Tube Side. The following symbols are used :—

T. Temperature of shell-side fluid at any point.
T_1 and T_2. Inlet and outlet temperatures of shell-side fluid.
t^I. Temperature of tube-side fluid at any point in the first pass.
t^{II}. Temperature of tube-side fluid at any point in the second pass.
t_1 and t_2. Inlet and outlet temperatures of tube-side fluid.
W. Weight of shell-side fluid passing per unit time.
w. Weight of tube-side fluid passing per unit time.
S. Specific heat of shell-side fluid.
s. Specific heat of tube-side fluid.
K. Overall coefficient of heat transfer.
l. Length of each pass.
x. Distance of any point from the end of the heat exchanger.
θ_m. Mean temperature difference for the heat exchanger.
n. Area of heating surface per unit length in each pass.

The heat exchanger is shown diagrammatically in Fig. 1.

A heat balance over the whole exchanger gives :

$$WS\,(T_1-T_2)=ws\,(t_2-t_1) \quad \ldots\ldots (1)$$

A heat balance over the right-hand section of the exchanger gives :

$$WS\,(T_1-T)=ws\,(t^{II}-t^I) \quad \ldots\ldots (2)$$

On differentiation this gives :

$$WS\,.\,\delta T = ws\,(\delta t^I-\delta t^{II}) \quad \ldots\ldots (3)$$

For the heat transfer across a small section of the exchanger, we have for the first pass :

$$ws\,.\,\delta t^I = Kn\,.\,\delta x\,(T-t^I) \quad \ldots\ldots (4)$$

and for the second pass :

$$-ws\,.\,\delta t^{II}=Kn\,.\,\delta x\,(T-t^{II}) \quad \ldots\ldots (5)$$

Substituting the values of δt^I and δt^{II} given by equations (4) and (5) in equation (3) :

$$WS\,.\,\delta T = ws\,(\delta t^I-\delta t^{II})=Kn\,.\,\delta x\,(2T-t^I-t^{II})$$

or

$$\frac{WS}{Kn}\cdot\frac{dT}{dx} = 2T-t^I-t^{II} \quad \ldots\ldots (6)$$

Differentiating this equation :

$$\frac{WS}{Kn}\cdot\frac{d^2T}{dx^2} = 2\frac{dT}{dx}-\frac{dt^I}{dx}-\frac{dt^{II}}{dx}$$

and since $$\frac{dt^I}{dx} = \frac{Kn}{ws}(T - t^I)$$

and $$\frac{dt^{II}}{dx} = -\frac{Kn}{ws}(T - t^{II})$$

$$\therefore \quad \frac{WS}{Kn} \cdot \frac{d^2T}{dx^2} = 2\frac{dT}{dx} - \frac{Kn}{ws}(t^{II} - t^I)$$

Then, using the value of $(t^{II} - t^I)$ from equation (2):

$$\frac{d^2T}{dx^2} - 2\frac{Kn}{WS} \cdot \frac{dT}{dx} + \frac{K^2n^2}{w^2s^2}(T_1 - T) = 0 \quad \ldots\ldots\ldots\ldots \quad (7)$$

Equation (7) is the differential equation giving the value of T at any point. If we put $T_1 - T = z$, so that

$$\frac{dT}{dx} = -\frac{dz}{dx} \text{ and } \frac{d^2T}{dx^2} = -\frac{d^2z}{dx^2}, \text{ then}$$

$$\frac{d^2z}{dx^2} - 2\frac{Kn}{WS} \cdot \frac{dz}{dx} - \frac{K^2n^2}{w^2s^2} \cdot z = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7a)$$

To solve this equation put $z = e^{mx}$.

Then $$m^2 - 2\frac{Kn}{WS} \cdot m - \frac{K^2n^2}{w^2s^2} = 0$$

and $$m = \frac{Kn}{WS} \pm \sqrt{\frac{K^2n^2}{W^2S^2} + \frac{K^2n^2}{w^2s^2}} = \frac{Kn}{WS}\left\{1 \pm \sqrt{1 + \frac{W^2S^2}{w^2s^2}}\right\}$$

Writing λ for $\sqrt{1 + \frac{W^2S^2}{w^2s^2}}$, then $m = \frac{Kn}{WS}(1 \pm \lambda)$

The solution of equation (7a) is then:

$$z = ae^{m_1x} + be^{m_2x} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

where $m_1 = \frac{Kn}{WS}(1 + \lambda)$ and $m_2 = \frac{Kn}{WS}(1 - \lambda)$ $\ldots\ldots\ldots$ (9)

and a and b are constants of integration.

These constants are determined by the conditions that when $x = o$, $T = T_2$ and $z = T_1 - T_2$ and when $x = l$, $T = T_1$ and $z = o$.

Applying these conditions to equation (8):

$$T_1 - T_2 = a + b$$

and $$o = ae^{m_1l} + be^{m_2l},$$

whence $$a = \frac{-(T_1 - T_2)\, e^{m_2l}}{e^{m_1l} - e^{m_2l}}$$

and $$b = \frac{(T_1 - T_2)\, e^{m_2l}}{e^{m_1l} - e^{m_2l}}$$

We thus obtain :

$$z = T_1 - T = \frac{(T_1 - T_2)}{e^{m_1 l} - e^{m_2 l}} (e^{m_1 l + m_2 x} - e^{m_2 l + m_1 x}) \quad \ldots\ldots\ldots (10)$$

where m_1 and m_2 have the values given by equation (9).

The temperature of the shell-side fluid at any point is given by this equation.

Differentiating equation (8) gives :

$$\frac{dz}{dx} = -\frac{dT}{dx} = am_1 e^{m_1 x} + bm_2 e^{m_2 x};$$

and using equation (6) we have :

$$am_1 e^{m_1 x} + bm_2 e^{m_2 x} = -\frac{Kn}{WS} (2T - t^I - t^{II}) \quad \ldots\ldots\ldots\ldots (10a)$$

When $x = o$, $T = T_2$, $t^I = t_1$ and $t^{II} = t_2$, so that

$$am_1 + bm_2 = -\frac{Kn}{WS} (2T_2 - t_1 - t_2).$$

Using the values given above for a, b, m_1, m_2,

$$\frac{T_1 - T_2}{e^{m_1 l} - e^{m_2 l}} \left\{ (1+\lambda) e^{m_2 l} - (1-\lambda) e^{m_1 l} \right\} = 2T_2 - t_1 - t_2$$

or $$\lambda (T_1 - T_2) \frac{(e^{m_1 l} + e^{m_2 l})}{e^{m_1 l} - e^{m_2 l}} = T_1 + T_2 - t_1 - t_2 \ldots\ldots\ldots (10b)$$

and $$e^{(m_1 - m_2)l} = \frac{T_1 + T_2 - t_1 - t_2 + \lambda (T_1 - T_2)}{T_1 + T_2 - t_1 - t_2 - \lambda (T_1 - T_2)}$$

and $$(m_1 - m_2) l = \log_e \left\{ \frac{T_1 + T_2 - t_1 - t_2 + \lambda (T_1 - T_2)}{T_1 + T_2 - t_1 - t_2 - \lambda (T_1 - T_2)} \right\} \ldots (10c)$$

Now $$(m_1 - m_2) l = \frac{2 Kn\lambda l}{WS}.$$

Also the total heat transferred in the exchanger is :

$$WS (T_1 - T_2) = 2 Knl\theta_m,$$

whence $$(m_1 - m_2) l = \frac{\lambda (T_1 - T_2)}{\theta_m}$$

The mean temperature difference θ_m is thus given by the equation :

$$\frac{\lambda (T_1 - T_2)}{\theta_m} = \log_e \left\{ \frac{T_1 + T_2 - t_1 - t_2 + \lambda (T_1 - T_2)}{T_1 + T_2 - t_1 - t_2 - \lambda (T_1 - T_2)} \right\} \ldots\ldots (11)$$

This equation gives θ_m in terms of the inlet and outlet temperatures of the two fluids and the factor λ.

Now $\lambda = \sqrt{1 + \frac{W^2 S^2}{w^2 s^2}} = \sqrt{1 + \frac{(t_2 - t_1)^2}{(T_1 - T_2)^2}}$ from equation (1)

so that $\lambda\,(T_1-T_2) = \sqrt{(T_1-T_2)^2+(t_2-t_1)^2}$

and equation (11) becomes

$$\frac{\sqrt{(T_1-T_2)^2+(t_2-t_1)^2}}{\theta_m} =$$

$$\log_e\left\{\frac{T_1+T_2-t_1-t_2+\sqrt{(T_1-T_2)^2+(t_2-t_1)^2}}{T_1+T_2-t_1-t_2-\sqrt{(T_1-T_2)^2+(t_2-t_1)^2}}\right\} \quad \ldots\ldots\ldots \quad (12)$$

When W or w becomes very large so that $T_1=T_2$ or $t_1=t_2$, then equation (12) reduces to the ordinary logarithmic mean formula.

It is of interest to compare the mean temperature difference given by equation (11) with that obtaining in a single-pass heat exchanger with the same inlet and outlet temperatures. In the latter case, for counter-current flow, the inlet and outlet temperature differences are :

$$\theta_1=T_1-t_2 \text{ and } \theta_2=T_2-t_1$$

and the mean temperature difference, θ_e is given by :

$$\theta_e = \frac{\theta_1-\theta_2}{\log_e\frac{\theta_1}{\theta_2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

If we put $\frac{WS}{ws}=R$ so that $R\,(T_1-T_2) = t_2-t_1$,

then $\theta_1-\theta_2=T_1-t_2-(T_2-t_1)=T_1-T_2-(t_2-t_1)=(1-R)\,(T_1-T_2)$.

Equation (12) then becomes

$$\frac{\sqrt{1+R^2}}{1-R}\cdot\frac{\theta_1-\theta_2}{\theta_m} = \log_e\left\{\frac{\theta_1+\theta_2+\frac{\sqrt{1+R^2}}{1-R}(\theta_1-\theta_2)}{\theta_1+\theta_2-\frac{\sqrt{1+R^2}}{1-R}(\theta_1-\theta_2)}\right\}$$

Putting $\eta = \frac{\sqrt{1+R^2}}{1-R}$,

$$\theta_m = \frac{\eta\,(\theta_1-\theta_2)}{\log_e\left\{\frac{\theta_1(\eta+1)-\theta_2(\eta-1)}{\theta_2(\eta+1)-\theta_1(\eta-1)}\right\}}$$

The ratio of θ_m and θ_e, the mean temperature difference in the two exchangers, is :

$$\frac{\theta_m}{\theta_e} = \frac{\eta\log_e\frac{\theta_1}{\theta_2}}{\log_e\left\{\frac{\theta_1(\eta+1)-\theta_2(\eta-1)}{\theta_2(\eta+1)-\theta_1(\eta-1)}\right\}} \quad \ldots\ldots\ldots\ldots\ldots \quad (13a)$$

This ratio depends only on the ratio $\frac{\theta_1}{\theta_2}$ and the factor η.

It has been shown elsewhere[2] that the logarithmic mean, as given by equation (13), is also given with good approximation by the equation :

$$2\sqrt[3]{\theta_e} = \sqrt[3]{\theta_1} + \sqrt[3]{\theta_2}$$

Comparing equations (11) and (13) and using the same method, we obtain from equation (11) the approximate equation :

$$2\sqrt[3]{\theta_m} = \sqrt[3]{\tfrac{1}{2}\{T_1+T_2-t_1-t_2+\lambda(T_1-T_2)\}} + \sqrt[3]{\tfrac{1}{2}\{T_1+T_2-t_1-t_2-\lambda(T_1-T_2)\}} \quad \ldots\ldots\ldots\ldots (14)$$

The temperature, t_c, of the tube fluid at the end of the first pass can be found as follows. When $x=l$, $T=T_1$ and $t^I=t^{II}=t_c$. Substituting these values in equation (10*a*) gives :

$$-2\frac{Kn}{WS}(T_1-t_c) = am_1e^{m_1l} + bm_2e^{m_2l}$$

Using the values previously found for a, b, m_1, m_2, we obtain, after some simplification :

$$2\lambda \log\{2(T_1-t_c)\} = (\lambda+1)\log\{T_1+T_2-t_1-t_2+\lambda(T_1-T_2)\} + (\lambda-1)\log\{T_1+T_2-t_1-t_2-\lambda(T_1-T_2)\} \quad \ldots\ldots\ldots (15)$$

from which t_c is readily calculated.

The temperature of the shell-side fluid at any point in the exchanger is given by equation (10). The temperature of the tube-side fluid at any point can be found by integrating equation (4) or (5). Writing equation (4) in the form :

$$\frac{dt^I}{dx} + \frac{Kn}{ws}\cdot t^I = \frac{Kn}{ws}\cdot T$$

and multiplying both sides of the equation by $e^{\frac{Knx}{ws}}$, we have

$$\frac{d}{dx}\left(t^I \cdot e^{\frac{Knx}{ws}}\right) = \frac{Kn}{ws}\cdot T\cdot e^{\frac{Knx}{ws}}$$

$$\text{and } t^I \cdot e^{\frac{Knx}{ws}} = \int \frac{Kn}{ws}\cdot T\,.\,e^{\frac{Knx}{ws}}\cdot dx + \text{constant.}$$

Since T is given as an exponential function of x by equation (10), the expression on the right-hand side of the above equation is readily integrated. The constant of integration is then determined from the condition that $t^I=t_1$ when $x=0$. By a similar procedure equation (5) can be integrated to give the temperature of the tube-side fluid at any point in the second pass.

[2] Underwood, *Industrial Chemist*, 1933, p. 169.

When the flow of the shell-side fluid as shown in Fig. 1 is reversed to give the arrangement shown in Fig. 2, slightly different equations

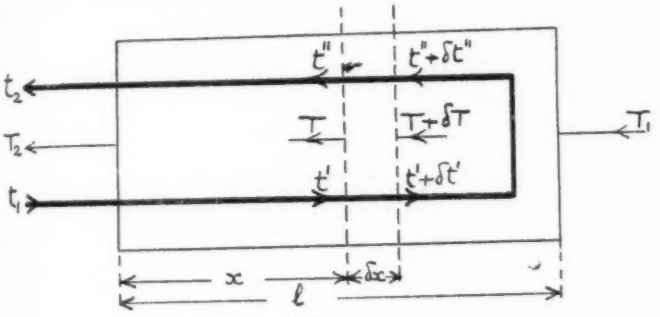

FIG 1.

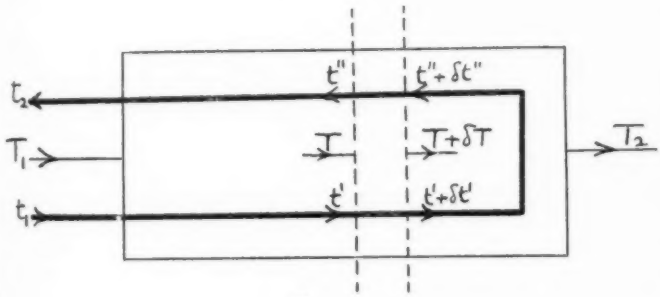

FIG. 2

are obtained. Equations (1), (3), (4) and (5) remain the same, but equation (2) now becomes :

$$WS\,(T-T_2) = ws\,(t^{II}-t^{I}).$$

Proceeding as before we obtain the differential equation :

$$\frac{d^2T}{dx^2}+2\frac{Kn}{WS}\cdot\frac{dT}{dx}-\frac{K^2n^2}{w^2s^2}(T-T_2)=0.$$

Putting $T-T_2=z$, we have :

$$\frac{d^2z}{dx^2}+2\frac{Kn}{WS}\cdot\frac{dz}{dx}-\frac{K^2n^2}{w^2s^2}\cdot z=0.$$

This differential equation is solved exactly as before, the conditions now being that $T=T_1$ when $x=0$ and $T=T_2$ when $x=l$.

It is found that the mean temperature difference is again given by equations (11) or (12), which thus holds good for both cases. The temperature of the tube fluid, t_c, at the end of the first pass, is now given by the equation :

$$2\lambda \log\{2(T_2-t_c)\} = (\lambda+1)\log\{T_1+T_2-t_1-t_2-\lambda(T_1-T_2)\} + (\lambda-1)\log\{T_1+T_2-t_1-t_2+\lambda(T_1-T_2)\} \quad \ldots\ldots\ldots (16)$$

which differs from equation (15).

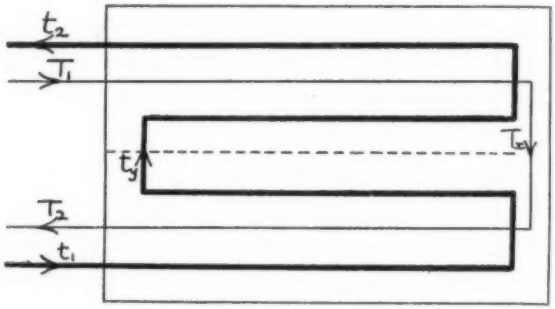

FIG. 3

Two Passes on the Shell Side, Four Passes on the Tube Side.— This arrangement is shown in Fig. 3. It is assumed that the heat transfer through the longitudinal baffle can be neglected. The temperature of the shell-side fluid on passing from one section of the exchanger to the other is denoted by T_x. The corresponding temperature of the tube-side fluid is denoted by t_y. Applying equation (10c) to the two sections of the exchanger we obtain :

$$\log_e\left\{\frac{T_1+T_x-t_y-t_2+\lambda(T_1-T_x)}{T_1+T_x-t_y-t_2-\lambda(T_1-T_x)}\right\} = 2\frac{Kn\lambda l}{WS} \quad \ldots\ldots\ldots (17)$$

$$\text{and } \log_e\left\{\frac{T_x+T_2-t_1-t_y+\lambda(T_x-T_2)}{T_x+T_2-t_1-t_y-\lambda(T_x-T_2)}\right\} = 2\frac{Kn\lambda l}{WS} \quad \ldots\ldots\ldots (18)$$

It is now necessary to eliminate the unknown temperatures T_x and t_y from the above equations. For this purpose we can use the two equations obtained by taking a heat balance for each section of the exchanger. Putting $\frac{WS}{ws} = R$, we have :

$$(t_y-t_1) = R(T_x-T_2) \quad \ldots\ldots\ldots (19)$$

$$\text{and } (t_2-t_y) = R(T_1-T_x) \quad \ldots\ldots\ldots (20)$$

From equations (17) and (18), putting $\psi = 2\,\frac{\mathrm{Kn}\lambda l}{\mathrm{WS}}$, we have:

$$\frac{T_1+T_x-t_y-t_2}{T_1-T_x} = \lambda \cdot \frac{e^{\psi}+1}{e^{\psi}-1}$$

and

$$\frac{T_x+T_2-t_1-t_y}{T_x-T_2} = \lambda \cdot \frac{e^{\psi}+1}{e^{\psi}-1}$$

Denoting by F the expression $\lambda \cdot \frac{e^{\psi}+1}{e^{\psi}-1}$, then

$$F\,(T_1-T_x) = T_1+T_x-t_y-t_2$$

and

$$F\,(T_x-T_2) = T_x+T_2-t_1-t_y.$$

Subtracting these two equations:

$$F\,(T_1-2\,T_x+T_2) = T_1-T_2+t_1-t_2 \quad \ldots\ldots\ldots\ldots \quad (21)$$

Adding these two equations:

$$F\,(T_1-T_2) = T_1+2\,T_x+T_2-t_1-2\,t_y-t_2$$

or

$$F\,(T_1-T_2) = 2(T_1+T_2-t_1-t_2)-(T_1-2T_x+T_2)+ (t_1-2\,t_y+t_2) \quad \ldots\ldots\ldots\ldots \quad (22)$$

By subtraction of equations (19) and (20):

$$t_1-2t_y+t_2 = R\,(T_1-2T_x+T_2),$$

so that equation (22) becomes:

$$F(T_1-T_2) = 2\,(T_1+T_2-t_1-t_2) + (R-1)\,(T_1-2T_x+T_2) \ldots (22a)$$

Eliminating the term containing T_x from equations (21) and (22*a*):

$$F^2(T_1-T_2) - 2F\,(T_1+T_2-t_1-t_2) + (1-R)\,(T_1-T_2+t_1-t_2) = 0.$$

Since

$$R\,(T_1-T_2) = t_2-t_1$$

$\therefore$

$$1-R = \frac{T_1-T_2+t_1-t_2}{T_1-T_2},$$

so that

$$F^2\,(T_1-T_2)-2F(T_1+T_2-t_1-t_2) + \frac{(T_1-T_2+t_1-t_2)^2}{T_1-T_2} = 0$$

Solving this equation gives:

$$F = \frac{(T_1+T_2-t_1-t_2) \pm 2\sqrt{(T_1-t_2)\,(T_2-t_1)}}{T_1-T_2} = \lambda \cdot \frac{e^{\psi}+1}{e^{\psi}-1}$$

It can be shown that the positive sign must be taken in order that the above equation should reduce to the logarithmic mean formula when $T_1=T_2$ or $t_1=t_2$. Consequently:

$$\frac{e^{\psi}+1}{e^{\psi}-1} = \frac{T_1+T_2-t_1-t_2+2\sqrt{(T_1-t_2)\,(T_2-t_1)}}{\lambda(T_1-T_2)}$$

and

$$e^{\psi} = \frac{T_1+T_2-t_1-t_2+2\sqrt{(T_1-t_2)\,(T_2-t_1)}+\lambda(T_1-T_2)}{T_1+T_2-t_1-t_2+2\sqrt{(T_1-t_2)\,(T_2-t_1)}-\lambda(T_1-T_2)}$$

Now $\psi = \dfrac{2\,\mathrm{Kn}\lambda l}{\mathrm{WS}}$ and the mean temperature difference for the whole exchanger is given by :

$$4\mathrm{Kn}l\theta_m = \mathrm{WS}\,(T_1 - T_2)$$

so that

$$\psi = \frac{\lambda\,(T_1 - T_2)}{2\theta_m}$$

The mean temperature difference is therefore given by the equation :

$$\frac{\lambda(T_1-T_2)}{2\theta_m} =$$

$$\log_e\left\{\frac{T_1+T_2-t_1-t_2+2\sqrt{(T_1-t_2)(T_2-t_1)}+\lambda(T_1-T_2)}{T_1+T_2-t_1-t_2+2\sqrt{(T_1-t_2)(T_2-t_1)}-\lambda(T_1-T_2)}\right\} \quad .. \quad (23)$$

$$\text{or}\ \frac{\lambda(T_1-T_2)}{2\theta_m} = \log_e\left\{\frac{(\sqrt{T_1-t_2}+\sqrt{T_2-t_1})^2+\lambda(T_1-T_2)}{(\sqrt{T_1-t_2}+\sqrt{T_2-t_1})^2-\lambda(T_1-T_2)}\right\} \quad .. \quad (24)$$

Since $\lambda(T_1-T_2) = \sqrt{(T_1-T_2)^2+(t_2-t_1)^2}$, equation (24) may be written :

$$\frac{\sqrt{(T_1-T_2)^2+(t_2-t_1)^2}}{2\theta_m} =$$

$$\log_e\left\{\frac{(\sqrt{T_1-t_2}+\sqrt{T_2-t_1})^2+\sqrt{(T_1-T_2)^2+(t_2-t_1)^2}}{(\sqrt{T_1-t_2}+\sqrt{T_2-t_1})^2-\sqrt{(T_1-T_2)^2+(t_2-t_1)^2}}\right\} \quad .. \quad (25)$$

The mean temperature difference thus depends not only on the inlet and outlet temperature differences (T_1-t_2) and (T_2-t_1), as

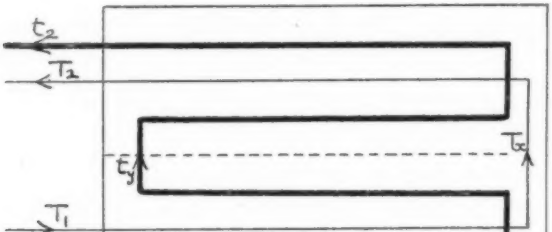

FIG. 4

in ordinary counter-current flow, but also on the change in temperature of each fluid as it passes through the exchanger. It can be shown, by the same method used for deriving equation (13*a*), that

the ratio of the mean temperature difference to the logarithmic mean depends only on the ratio θ_1/θ_2 and the factor η.

If the flow of the shell-side fluid, as shown in Fig. 3, is reversed to give the arrangement shown in Fig. 4, it can be shown by the same method as was used above, that instead of equation (24) we then have :

$$\frac{\lambda(T_1-T_2)}{2\theta_m}=\log_e\left\{\frac{(\sqrt{T_1-t_1}+\sqrt{T_2-t_2})^2+\lambda(T_1-T_2)}{(\sqrt{T_1-t_1}+\sqrt{T_2-t_2})^2-\lambda(T_1-T_2)}\right\} \quad \ldots\ldots (26)$$

One Pass on the Shell Side, Four Passes on the Tube Side.— This arrangement is shown in Fig 5. The temperatures of the tube fluid in the different passes are denoted by t^{I}, t^{II}, t^{III} and t^{IV}

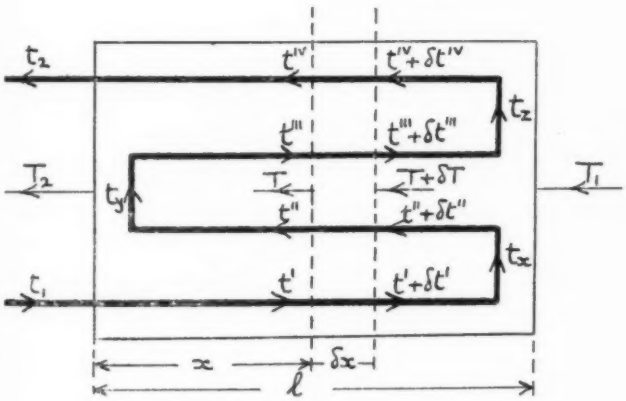

FIG. 5

respectively. The temperatures of the tube fluid between successive passes are denoted by t_x, t_y, t_z as shown in Fig. 5. A heat balance for the right-hand section of the exchanger gives :

$$WS\,(T_1-T) = ws\,(t^{II}-t^{I}+t^{IV}-t^{III}) \quad \ldots\ldots (27)$$

from which, by differentiation,

$$WS\cdot\delta T = ws\,(\delta t^{I}-\delta t^{II}+\delta t^{III}-\delta t^{IV}) \quad \ldots\ldots (28)$$

For the heat transfer across a small section of the exchanger, we have for the four passes :

$$ws\cdot\delta t^{I}=Kn\cdot\delta x\,(T-t^{I}) \quad \ldots\ldots (29a)$$

$$-ws\cdot\delta t^{II}=Kn\cdot\delta x\,(T-t^{II}) \quad \ldots\ldots (29b)$$

$$ws\cdot\delta t^{III}=Kn\cdot\delta x\,(T-t^{III}) \quad \ldots\ldots (29c)$$

$$-ws\cdot\delta t^{IV}=Kn\cdot\delta x\,(T-t^{IV}) \quad \ldots\ldots (29d)$$

Combining equation (28) with equations (29*a*) to (29*d*) :

$$WS \cdot \delta T = ws(\delta t^{I} - \delta t^{II} + \delta t^{III} - \delta t^{IV}) = Kn \cdot \delta x\,(4T - t^{I} - t^{II} - t^{III} - t^{IV})$$

or $$\frac{WS}{Kn} \cdot \frac{dT}{dx} = 4T - t^{I} - t^{II} - t^{III} - t^{IV} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (30)$$

Differentiating this equation gives :

$$\frac{WS}{Kn} \cdot \frac{d^2T}{dx^2} = 4 \cdot \frac{dT}{dx} - \frac{dt^{I}}{dx} - \frac{dt^{II}}{dx} - \frac{dt^{III}}{dx} - \frac{dt^{IV}}{dx}$$

Substituting for $\frac{dt^{I}}{dx}$, etc., from equations (29*a*) to 29*d*)

$$\frac{WS}{Kn} \cdot \frac{d^2T}{dx^2} = 4 \cdot \frac{dT}{dx} - \frac{Kn}{ws}\,(t^{II} - t^{I} + t^{IV} - t^{III})$$

and from equation (27)

$$\frac{WS}{Kn} \cdot \frac{d^2T}{dx^2} = 4 \cdot \frac{dT}{dx} - \frac{Kn}{ws} \cdot \frac{WS}{ws}\,(T_1 - T) \quad \ldots\ldots\ldots\ldots\ldots \quad (30)$$

Putting $T_1 - T = z$, the equation becomes :

$$\frac{d^2z}{dx^2} - 4 \cdot \frac{Kn}{WS} \cdot \frac{dz}{dx} - \frac{K^2n^2}{w^2s^2} \cdot z = 0 \quad \ldots\ldots\ldots\ldots\ldots \quad (30a)$$

The solution of this equation is obtained by putting $z = e^{mx}$, so that

$$m^2 - 4\frac{Kn}{WS} \cdot m - \frac{K^2n^2}{w^2s^2} = 0$$

and $$m = 2\frac{Kn}{WS}\left(1 \pm \sqrt{1 + \frac{W^2S^2}{4w^2s^2}}\right)$$

Writing $\mu = \sqrt{1 + \frac{W^2S^2}{4w^2s^2}}$ and $m_1 = 2\frac{Kn}{WS}(1+\mu)$ and $m_2 = 2\frac{Kn}{WS}(1-\mu)$

the solution of equation (30*a*) is :

$$z = a \cdot e^{m_1 x} + be^{m_2 x} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (31)$$

The constants of integration a and b are determined by the conditions that when $x = 0$, $z = T_1 - T_2$ and when $x = l$, $z = 0$, so that

$$T_1 - T_2 = a + b$$

and $$0 = ae^{m_1 l} + be^{m_2 l},$$

whence $$a = -\frac{(T_1 - T_2)e^{m_2 l}}{e^{m_1 l} - e^{m_2 l}} \text{ and } b = \frac{(T_1 - T_2)e^{m_1 l}}{e^{m_1 l} - e^{m_2 l}} \quad \ldots\ldots\ldots \quad (32)$$

Using the same method to find the mean temperature difference as was used for the heat exchanger with one shell-side pass and two tube-side passes, we have, from equations (30) and (31) :

$$\frac{dT}{dx} = \frac{Kn}{WS}(4T - t^{I} - t^{II} - t^{III} - t^{IV}) = -\frac{dz}{dx} = -am_1e^{m_1 x} - bm_2e^{m_2 x} \quad (33)$$

When $x=O,\ T=T_2,\ t^I=t_1,\ t^{II}=t^{III}=t_y,\ t^{IV}=t_2,$

so that

$$\frac{Kn}{WS}(4T_2-t_1-2t_y-t_2)=-am_1-bm_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots(34)$$

The temperature, ty, between the second and third passes is not yet known. It can be determined in the following manner :— Subtracting equations (29*a*) and (29*c*)

$$ws\,(\delta t^I-\delta t^{II})=-Kn\cdot\delta x\,(t^I-t^{III})$$

or

$$\frac{d(t^I-t^{III})}{t^I-t^{II}}=-\frac{Kn}{ws}\cdot dx$$

Integrating

$$t^I-t^{III}=C\cdot e^{\frac{-Knx}{ws}}$$

When $x=o,\ t^I=t_1$ and $t^{III}=t_y$ so that $C=t_1-t_y$

When $x=l,\ t^I=t_x$ and $t^{III}=t_z$ so that

$$t_x-t_z=(t_1-t_y)e^{\frac{-Knl}{ws}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (35)$$

Similarly from equations (29*b*) and (29*d*) :

$$\frac{d\,(t^{II}-t^{IV})}{t^{II}-t^{IV}}=\frac{Kn}{ws}\cdot dx$$

and

$$t^{II}-t^{IV}=C\cdot e^{\frac{Knx}{ws}}$$

When $x=O,\ t^{II}=t_y$ and $t^{IV}=t_2$ so that $C=t_y-t_2$.

When $x=l,\ t^{II}=t_x$ and $t^{IV}=t_z$, so that

$$t_x-t_z=(t_y-t_2)\,e^{\frac{Knl}{ws}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (36)$$

Eliminating t_x and t_z from equations (35) and (36) gives :

$$t_y=\frac{t_1+t_2\cdot e^{\frac{2Knl}{ws}}}{1+e^{\frac{2Knl}{ws}}}$$

Substituting this value of t_y in equation (34) and using the values previously found for a, b, m_1 and m_2, we obtain, after some simplification :

$$2\mu(T_1-T_2)\frac{e^{\frac{4Kn\mu l}{ws}}+1}{e^{\frac{4Kn\mu l}{ws}}-1}+(t_2-t_1)\frac{e^{\frac{2Knl}{ws}}-1}{e^{\frac{2Knl}{ws}}+1}=2(T_1+T_2-t_1-t_2)$$

Using hyperbolic instead of exponential functions :

$$2\mu(T_1-T_2)\coth\left(\frac{2Kn\mu l}{ws}\right)+(t_2-t_1)\tanh\left(\frac{Knl}{ws}\right)=2(T_1+T_2-t_1-t_2)$$

From the relations

$$WS\,(T_1-T_2) = ws\,(t_2-t_1) = 4nlK\theta_m$$

we have

$$2\mu(T_1-T_2)\coth\left\{\frac{\mu(T_1-T_2}{2\theta_m}\right\}+(t_2-t_1)\tanh\left\{\frac{t_2-t_1}{4\theta_m}\right\} =$$
$$2\,(T_1+T_2-t_1-t_2) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (37)$$

From this equation, the value of θ_m can be found by trial and error solution. The equation may be written in the form :

$$\frac{\mu(T_1-T_2)}{2\theta_m}\coth\left\{\frac{\mu(T_1-T_2)}{2\theta_m}\right\}+\frac{(t_2-t_1)}{4\theta_m}\tanh\left\{\frac{t_2-t_1}{4\theta_m}\right\} =$$
$$\frac{T_1+T_2-t_1-t_2}{2\theta_m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (37a)$$

In this form the computation of the left hand side of the equation for trial solutions of θ_m is easier than in the previous form, particularly if curves are plotted for $y=x\coth x$ and $y=x\tanh x$.

The second term on the left-hand side of the equation is always smaller than the first term. If this second term is neglected, as an approximation, the equation reduces to :

$$\frac{\mu(T_1-T_2)}{\theta_m} = \log_e\left\{\frac{T_1+T_2-t_1-t_2+\mu(T_1-T_2)}{T_1+T_2-t_1-t_2-\mu(T_1-T_2)}\right\} \quad \ldots\ldots\ldots \quad (38)$$

It will be observed that this is the same as equation (11) for the exchanger with one shell-side pass and two tube-side passes with the substitution of :

$$\mu=\sqrt{1+\frac{W^2S^2}{4w^2s^2}} \text{ for } \lambda=\sqrt{1+\frac{W^2S^2}{w^2s^2}}$$

If the flow of the shell-side fluid is in the opposite direction to that shown in Fig. 5, equations (37) and (38) still hold good.

As a numerical example to illustrate the variation in the mean temperature difference in the types of heat exchanger discussed take the values :

$$T_1=385^\circ\text{ F}, T_2=235^\circ\text{ F}, t_1=200^\circ\text{ F}, t_2=250^\circ\text{ F}.$$

The figures shown below give the mean temperature differences in the various cases compared with that obtaining with ordinary counter-current flow where the logarithmic mean applies :

	θ_m	Ratio.
Counter-current flow (log. mean) ..	74·1° F. ..	1
One-two pass exchanger	47·7 ..	0·64
Two-four pass exchanger	69·6 ..	0·94
One-four pass exchanger	45·6 ..	0·62

The Determination of Specific Refraction and Other Constants[1] as Means of Following the Course of the Treatment of Heavy Oils by the Edeleanu Process.*

By Professor H. I. Waterman, Ph.D. (Hon. Member), P. C. Kruijff, W. J. K. Schönlau, and A. J. Tulleners (Student Member).

Summary.

In the example given, the average number of rings per molecule in the extract and in the refined product is about equal and does not differ materially from that of the charging stock. This was proved by the application of a new method of examining mineral oils (specific refraction, molecular weight, aniline point).

The differences between the refined product and the extract can be ascribed to the higher percentage of aromatic rings in the extract. The average molecular weight of the refined product is higher, and therefore the paraffinic side chains are longer or more numerous.

For the purpose of this investigation a Borneo oil distillate was used, of which 4 per cent. by volume boiled below 220° C. and 33 per cent. between 220° and 300° C. A semi-commercial distillation was carried out and three lubricating oil distillates obtained, the properties of which were as follows :—

Quantity. Kg.	n_D^{20}	d_4^{20}	Mean molecular weight (benzene).
2·1	1·5631	0·9962	326
3·3	1·5639	1·0001	359
2·0	1·5643	1·0042	377
7·4	1·5642	0·9995	342

Of this mixture 6·4 kg. was used as charging stock and subjected to an extraction with liquid SO_2 by the Edeleanu process.

A small percentage of benzene was added, the mixture placed in glass Dewar flasks and 250-ml. portions were subjected to three treatments with 250 ml. of a mixture of liquid SO_2 and C_6H_6 (95 vol. : 5 vol.). The refined product amounted to 2·45 kg. (38·2 per cent.), and the extract to 3·55 kg. (55·3 per cent.), the loss being 0·42 kg.

	Charging stock.	Extract.	Refined product.
n_D^{20}	1·5642	1·59	—
n_D^{50}	—	—	1·5077
d_4^{20}	0·9995	1·0399	—
d_4^{50}	—	—	0·9290
Mean molecular weight (benzene)	342	317	398
Sulphur, per cent.	0·30	0·48	0·11
Aniline Point, °C.	40·0	about −15	75·2

* Paper received November 30, 1933.

[1] J. C. Vlugter, H. I. Waterman and H. A. Van Westen. "Improved Methods of Examining Mineral Oils, especially the High-boiling Components of Non-Aromatic Character," *J. Inst. Petr. Techn.*, 1932, **18**, 735–750 ; *Chem. Weekbl.*, 1932, **29**, 226 ; see also J. C. Vlugter, "Dissertation," Delft, 1932.

The properties of the charging stock, refined product and extract are given in the preceding table.

The charging stock, the refined product and the extract were submitted to a cathodic light vacuum distillation[2] with internal condensation, and the results are given below :—

		n_D^{20}	d_4^{20}	Molecular weight (benzene).	Aniline point, °C.
Charging Stock (191 *ml.*) :—					
Fraction I (30 ml.)	..	1·5654	1·0005	287	20·2
,, II ,,	..	1·5690	1·0048	320	26·2
,, III ,,	..	1·5668	1·0033	336	32·5
,, IV ,,	..	1·5640	1·0005	354	35·0
,, V ,,	..	1·5610	0·9978	377	43·8
,, VI ,,	..	1·5594	—	383	—
Residue	..	—	—	—	—
Refined Product (150 *ml.*) :—					
Fraction I (20 ml.)	..	1·5141	0·9454	331	63·5
,, II ,,	..	1·5198	0·9505	378	68·2
,, III ,,	..	1·5200	0·9501	399	72·2
,, IV ,,	..	1·5201	0·9503	418	76·4
,, V ,,	..	1·5099 (50°)	—	447	78·6
,, VI ,,	..	1·5085 (50°)	0·9359 (50°)	446	82·0
Residue	..	—	—	—	—
Extract (205 *ml.*) :—					
Fraction I (30 ml.)	..	1·5845	1·0163	262	—
,, II ,,	..	1·5973	1·0348	279	—
,, III ,,	..	1·6018	1·0399	293	—
,, IV ,,	..	1·6032	1·0424	302	—
,, V ,,	..	1·6033	1·0377	319	—
,, VI ,,	..	1·600	1·0437	344	—
Residue	..	—	1·068	374 (naphthalene)	—

In order to render more effective the analytical research on the charging stock, the hydrogenations of the extract and of the refined product were carried out under high hydrogen pressure, using nickel on a support of guhr as a catalyst. During the hydrogenation, care was taken that the temperature was kept relatively low, *i.e.*, below 310° C., and the process was carried out in several stages in order that the poisoned[3] catalyst could be changed each time and replaced by a new one. The charging stock was completely hydrogenated in eleven stages, the extract in thirteen stages, and the refined product in four stages. In special cases it might be useful to give a pretreatment with molten sodium

[2] H. I. Waterman and E. B. Elsbach, *Chem. Weekbl.*, 1929, **26**, 469; H. I. Waterman and J. N. J. Perquin, *Technische Analysen*, 4th edition, G. van Herwijnen, Dordrecht, 1931; H. I. Waterman, *Chem. Weekbl.*, 1933, **30**, 174.

[3] In connection with the sulphur content of the oils.

Properties of the Charging Stock, Refined Product and Extract and of the completely Saturated Hydr

	Ultimate Analysis.			n_D^t	d^{t_4}	$\frac{n^2-1}{n^2+2}\frac{1}{d}$ (D)	
		%C.	%H.				
Charging stock	—	—	—	1·5642 (t = 20°)	0·9995 (t = 20°)	0·3255 (20°)	
Charging stock completely hydrogenated.	Observed Calculated*	86·5 87·0	13·0 13·0	n_C : 1·4973 (t = 20°) n_D : 1·5001 (t = 20°) n_F : 1·5063 (t = 20°) n_G[1]: 1·5115 (t = 20°)	0·9281 (t = 20°)	0·3170 (20°)	the a
Refined product	Observed	87·7	12·1	n_D : 1·5077 (t = 50°)	0·9290 (t = 50°)	0·3207 (50°, 0·3199 (20°) (calculated)	
Refined product completely hydrogenated.	Observed Calculated*	86·3 86·8	13·3 13·2	n_D : 1·4843 (t = 50°) n_C : 1·4752 (t = 70°) n_D : 1·4777 (t = 70°) n_F : 1·4836 (t = 70°) n_G[1]: 1·4884 (t = 70°)	0·8962 (t = 50°) 0·8842 (t = 70°)	0·3194 (50°) 0·3186 (20°, (calculated) 0·3200 (70°) 0·3187 (20°) (calculated)	
Extract	Observed	89·6	8·7	n_D : 1·59 (t = 20°)	1·0399 (t = 20°)	—	
Extract completely hydrogenated	Observed Calculated*	86·9 87·0	12·7 13·0	n_C : 1·4979 (t = 20°) n_D : 1·5005 (t = 20°) n_F : 1·5069 (t = 20°) n_G[1]: 1·5124 (t = 20°)	0·9272 (t = 20°)	0·3175 (20°)	

* From the observed

and of the completely Saturated Hydrocarbon Mixtures obtained by Hydrogenation at Low Temperature us

	d^{t}_{4}	$\frac{n^2-1}{n^2+2}\frac{1}{d}$ (D)	Molecular Weight (Benzene used as a Solvent).	Sulphur. %	Aniline Point.		$\frac{n_G - n_C}{d} 10^4$	Naphthenic Rings. %	
					Observed. °C.	Read from Graph °C.			
°)	0·9995 (t = 20°)	0·3255 (20°)	342	0·30	40·0	—	—	25	
°) °) °) °)	0·9281 (t = 20°)	0·3170 (20°)	342 (naphthalene used a solvent)	—	87·8	86·5	152	65	
°)	0·9290 (t = 50°)	0·3207 (50°, 0·3199 (20°) (calculated)	398	0·11	75·2	—	—	39	
°) °) °) °) °)	0·8962 (t = 50°) 0·8842 (t = 70°)	0·3194 (50°) 0·3186 (20°, (calculated) 0·3200 (70°) 0·3187 (20°) (calculated)	373	—	96·4	93	149	57	
°)	1·0399 (t = 20°)	—	317	0·48	about − 15	—	—	10	
°) °) °) °)	0·9272 (t = 20°)	0·3175 (20°)	306	—	79·0	82	157	66	

* From the observed value of $\frac{n^2-1}{n^2+2}\frac{1}{d}$

Temperature using Nickel on Guhr as a Catalyst.

Naphthenic Rings. %	Paraffinic Chains. %	Percentage of Aromatic Rings calculated from			Average number of Rings per Molecule.
		Ultimate Analysis.	Gross Hydrogen consumption.	A.P. differences factor 0·83.[1]	
25	35	—	—	40	—
65	35	—	—	—	3·7
39	43	18	16	—	—
57	43	—	—	—	3·6
10	34	56	(75)		—
66	34	—	—	—	3·4

under a hydrogen pressure of 40 kg./cm.^{2} at about 300° C.,[4] in order that time could be saved by a reduction in the number of stages, of hydrogenation. By pretreating in this way it was possible to reduce the hydrogenation of the refined product to three stages without affecting the final product. By pretreating the extract in the same way it might be possible to obtain better practical results.

In the hydrogenation of the extract (temperature <310° C.) the consumption of hydrogen was about 5·8 per cent., and in the case of the refined product (temperature <300° C.) about 1·2 per cent. The hydrogenated products were completely saturated, as was proved by the value of the specific dispersion

$$\frac{n_{D1}-n_C}{d}\,10^4$$

and also by the small difference between the determined and the predicted aniline points.

From the results obtained it can be concluded that the average number of rings per molecule in the charging stock is about equal to the number in the extract and in the refined product. The differences between the extract and the refined product, therefore, are chiefly found in the percentage of aromatic rings and not in the average number of rings per molecule. In the extract the aromatic rings are present with only a small percentage of naphthenic rings and the ring systems have paraffinic side chains. In the refined product, a larger number of naphthenic rings are present with a smaller percentage of aromatic rings, while the paraffinic side chains are longer and more numerous. Only a small percentage of free paraffin wax was present in the refined product. The average molecular weight of the refined product was higher than that of the extract.

The methods developed give a better understanding of the features and principles of solvent extraction processes for the refining of oil, *e.g.*, the Edeleanu and similar processes.

It should be mentioned that there has been a tendency to study more thoroughly the solvent extraction processes, particularly during the past two years, and attention is directed to the work of Ferris and his collaborators.[5]

Laboratory of Chemical Engineering,
The University, Delft.

[4] See C. Ellis, "Hydrogenation of Organic Substances," 3rd edition, 1931, p. 568.

[5] The "Viscosity Gravity Constant" is used by this author to study the paraffinicity of lubricating oils. See S. W. Ferris, E. R. Birkhimer and L. M. Henderson, "Solvent Extraction of Lubricating Oils," *Ind. Eng. Chem.*, 1931, **23**, 753; S. W. Ferris and W. F. Houghton, "The Nitrobenzene Process for Lubricating Oils," World Petroleum Congress, 1933, **2**, 370.

The Destructive Hydrogenation of Phenyl-octadecane.*

By K. Laidler and A. Szayna.

Summary.

1. In the described conditions of destructive hydrogenation, the investigated hydrocarbons can be placed as follows, according to their decreasing thermal stability: benzene, toluene, phenyl-octadecane and octadecane.

2. In the phenyl-octadecane molecule the benzene ring is a far more stable component than the paraffinic side-chain.

3. At 440° C. phenyl-octadecane splits off the side-chain entirely or partly, yielding a small amount of gas and mainly liquids composed of benzene and its homologs and of paraffinic hydrocarbons. Besides these two classes of hydrocarbons there are also very small amounts of naphthenes and unsaturateds. The phenyl group is hydrogenated with difficulty.

4. Only at 470° C. does the rate of hydrogenation of aromatic nuclei increase and about one-third of the phenyl-octadecane is subject to hydrogenation in the phenyl group. Probably the naphthenic hydrocarbons obtained are further decomposed.

5. At elevated temperature of 490° C. phenyl-octadecane is split to a very large extent. Two-thirds of it appear in the form of gaseous molecules. Aromatics, *i.e.*, benzene and its low boiling homologs, being more stable than paraffinic hydrocarbons, are concentrated in the liquid fractions.

The aromatic hydrocarbons with long side-chains form a large proportion of the constituents of heavier cuts of petroleum oils. The study of their reactions to cracking and hydrogenation is of interest from the point of view of the manufacture of gasoline by these methods. Of this class of hydrocarbons, only toluene and p-cymene have been previously investigated.

According to Hofmann and Lang,[1] toluene, when hydrogenated at high temperature under high hydrogene pressure without catalysts, yields benzene and small amounts of di-tolyl and diphenyl; the main reaction being the splitting off the side-chain. Schoorel, Tulleners and Waterman[2] have subjected p-cymene to catalytic high pressure hydrogenation with nickel catalyst at 200° C., and have achieved the quantitative hydrogenation to p-menthane without the alteration of side-chains. This derivative of p-cymene loses the side-chains at 470° C. in the form of gas and yields mainly lower-boiling naphthenes.

The object of the present investigation was to study the reactions occurring when an aromatic hydrocarbon with long side-chain, such as phenyl-octadecane, is subjected to high pressure catalytic hydrogenation at elevated temperatures. For comparison, also, components and homologs of phenyl-octadecane—namely, n-octadecane, benzene and toluene—have been hydrogenated under identical conditions.

* Received July 20th, 1933.

[1] Hofmann and Lang, *Brenn.-Chem.*, 1929, **10**, 203.

[2] Schoorel, Tulleners and Waterman, 1932, *J. Inst. Petr. Techn.*, **18**, 179.

1-Phenyl-n-octadecane $C_6H_5 \cdot C_{18}H_{37}$ was obtained by the reaction of Wurtz according to Krafft[3]:

$$C_6H_5I + C_{18}H_{37}I + 2Na = C_6H_5 \cdot C_{18}H_{37} + 2NaI$$

The yield was 57 per cent. of the theoretical yield, and about 10 per cent. of n-hexa-triacontane, $C_{36}H_{74}$, and di-phenyl were also isolated from the products of this synthesis. n-Octadecane was obtained with 90·5 per cent. yield by dehydrating the stearylic alcohol $C_{18}H_{37}OH$ with phosphorus pentoxide and distilling off n-octadecene, the latter being hydrogenated at 180° C. under 50 atm. pressure with hydrogen in the presence of the nickel-alumina catalyst. The benzene and toluene were chemically pure products.

The properties of the starting materials were as follows:—

	1-Phenyl-n-octadecane $C_6H_5C_{18}H_{37}$	n-Octadecane $C_{18}H_{38}$	Benzene C_6H_6	Toluene $C_6H_5CH_3$
Melting Point, °C.	35	27	5·5	—
Boiling temp. ..	214°–220° by 1½ mm. Hg.	156°–160° by 3 mm. Hg.	80°	109·5–110°
Sp. Gr.	$0{\cdot}8510_4^{26}$	$0{\cdot}7768_4^{28}$	$0{\cdot}8796_4^{20}$	$0{\cdot}8660_4^{20}$
Refract. index ..	$1{\cdot}4751_D^{26}$	$1{\cdot}4367_D^{28}$	$1{\cdot}5011_D^{20}$	$1{\cdot}4958_D^{20}$
Iodine No. (Hanus)	0·0	1·3	—	—
Ultimate analysis:				
%C.	87·3	—	—	—
%H.	12·4	—	—	—

The hydrogenation of phenyl-octadecane was carried out in an electrically heated rotating autoclave of 2·5 litres capacity. Three experiments were made at 440°, 470° and 490° C., with an accuracy of 2° C. The time of reaction was 60 minutes. In each case 10 per cent. of the molybdenum sulphide catalyst[4] and 10 per cent. by weight of hydrogen at 110 atm. initial pressure were used. For comparison and easier interpretation of the results, n-octadecane at 440° and 490° C., and benzene and toluene at 490° C. were hydrogenated under identical conditions.

After cooling, the reaction gases were released from the bomb, and their volume and density measured. The liquid products, after filtration from the catalyst, were distilled with a 30 cm. tall Widmer column. The cuts were taken in the usual boiling ranges for lower aromatic hydrocarbons in order to separate one aromatic individual within the cut. Except in experiment No. 1 benzene and toluene were collected in one fraction 70–115° C. The specific gravity, refractive index, iodine number (Hanus) and absorption in three volumes of 100 per cent. sulphuric acid were determined. By the absorption the percentage of aromatics on the fraction and on the initial material was calculated. On the saturated residue after absorption of aromatics, the aniline point and also

[3] Krafft, *Ber.*, 1886, **19**, 2984.

[4] The catalyst was prepared by precipitation of ammonium sulphomolybdate with hydrochloric acid on the bleaching earth "Alsil," washing and drying at 105° in vacuo. It contained 35 per cent. of MoS_3.

the refractive index were determined, indicating approximately the content of naphthenic hydrocarbons. The average molecular weight of the distillation residue was determined by the cryoscopic method in naphthalene.

When pouring the liquid from the autoclave, the propane and butane dissolved in the liquid is volatilised during this operation and is included in the tables as "hydrogenation losses"; the remainder of the uncondensed gases was absorbed in charcoal absorbers.

From the data in the tables it is evident that with increase of temperature a greater decomposition of phenyl-octadecane takes place with formation of increasing amounts of gases and light cuts, and in consequence the heavy fractions disappear.

Phenyl-octadecane has on the aromatic nucleus a side-chain, an element of lower stability toward the action of heat. An idea of the relative thermal resistance of these two components is obtained by comparing experiments Nos. 5 and 7 carried out at 490° C. with benzene and n-octadecane. Benzene was not decomposed and only a small amount (3·5 per cent.) was hydrogenated to naphthenes, while octadecane was entirely split into gases and 12·65 per cent. of light liquid boiling within 19–150° C. Toluene, the next higher homolog of benzene, was less stable than benzene. Under the same conditions it undergoes a rupture of the methyl group in the side-chain, $C_6H_5CH_3 \xrightarrow{H_2} C_6H_6 + CH_4$, and a more pronounced hydrogenation of the nucleus takes place; it yielded approximately 25 per cent. of benzene and 5 per cent. naphthenes. The rest are mainly unchanged toluene and saturated hydrocarbons (gas).

From experiments 3, 5 and 6 it is seen that phenyl-octadecane, as regards thermal stability, occupies a position between toluene and paraffinic octadecane. Probably the phenyl group increases the stability of the side-chain. Nevertheless, it must be stated that an aromatic-paraffinic hydrocarbon decomposes easier when the side-chain is long. These hydrocarbons can be placed as follows, according to their decreasing thermal stability: benzene, $C_6H_6>$; toluene, $C_6H_5CH_3>$; phenyl-octadecane, $C_6H_5C_{18}H_{37}>$; octadecane, $C_{18}H_{38}$.

When investigating the reactions of cleavage of carbon bonds separately for the benzene ring and the paraffin side-chain, it must be remembered that phenyl-octadecane has six carbon atoms in the ring and eighteen in the chain. The nucleus, which is distinguished by the higher energy of the aromatic carbon bonds (96 Cal.) represents 23·3 per cent. on the whole molecule and is a component of higher thermal resistance, while the rest of the

molecule, 76·7 per cent. is the paraffinic radical $C_{18}H_{37}$ with lower energy of linkages (72 Cal.). This statement will simplify the understanding of the reactions of decomposition and hydrogenation.

The decomposition at 440° C. (experiment No. 1) yielded only a small amount of gas molecules, the liquid fractions boiling up to 200° C., being composed of aromatic and paraffinic hydrocarbons and very small quantities of naphthenes and unsaturated hydrocarbons. The aromatics are benzene[5] and homologs, probably up to $C_6H_5C_5H_{11}$. Higher homologs are present in the residue boiling above 200° C. In order to determine whether the benzene ring had undergone any transformation, the approximative content of the phenyl radical in all fractions was calculated. For example, in the cut 115–145° (experiment No. 1), containing 50 per cent. aromatics on the fraction or 3·87 per cent. on the initial material, it was considered that, by the boiling range, it represented the ethyl-benzene, or in terms of phenyl radical, 2·81 per cent. of this radical on the initial material. In the residue above 200° C. the same basis was calculated on the average molecular weight. In this way an approximative sum of phenyl groups in all fractions (22·4 per cent.) was obtained, and illustrated the higher resistance of this component of phenyl-octadecane. The aromatic ring in the conditions of experiment No. 1 is still very stable and is hydrogenated only to a very low degree; hence, very small amounts of naphthenes were found by the aniline point method. At 440° C. the side-chain is broken into smaller, mainly liquid, hydrocarbons, partly as free paraffins and partly as side-chains attached to the benzene ring.

The reaction rates increase at 470° C. (experiment No. 2), more gas and low-boiling liquids are formed, and the total phenyl groups are only about 17·4 per cent.; almost one-third loses its aromatic character by hydrogenation. The naphthenic hydrocarbons formed by hydrogenation of the benzene nuclei are detected in the liquids by the aniline point method, but it appeared impossible to calculate them with a satisfactory degree of accuracy. Nevertheless, all trial calculations indicated a deficiency of naphthenes; probably they had undergone further reactions of cleavage and hydrogenation with opening of the ring structure. There is also a possibility of isomerisation to penta-methylene rings. Evidence of such re-

[5] Benzene was identified by its crystalline compound $NiCy_2NH_3C_6H_6$ according to Hofmann and Höchtlen, *Ber.*, 1903, **36** 1149. Other homologs were determined quantitatively by the absorption in H_2SO_4 in the corresponding fractions: 70–90°=benzene, 90–115°=toluene, 115–145°=ethyl-benzene, 145–200°=propyl-to amyl-benzene (average $C_6H_5C_4H_9$).

Conditions of each Experiment: Time of Reaction: 60 min. 10 per cent. Catalyst; 10 per cent. by Weight Hydrogen under 110 atm. initial pressure.

Fraction.	Yield % weight.	D_4^{20}.	n_D^{20}.	Iodine No.	Per cent. of aromatic hydrocarb.		After absorb. in H_2SO_4.		Approx. content of phenyl radicals %	Mol. weight.
					On fraction.	On initial material.	n_D^{20}.	Aniline point °C.		
Experiment 1.—Phenyl-octadecane at 440° C.; pressure at react. temp. 252 atm.; after cooling 93 atm.										
Hydrocarbon gas	4·25	—	—	—	—	—	—	—	—	—
Hydrogenation loss	3·80	—	—	—	—	—	—	—	—	—
Charcoal absorb.	0·68	—	—	—	—	—	—	—	—	—
28–70°	3·52	0·6695	1·3875	8·2	9·0	0·31	—	—	0·31	—
70–115°	8·74	0·7610	1·4339	5·6	42·5	3·71	1·3903	67·7	3·36	—
115–145°	7·74	0·7902	1·4518	5·5	50·0	3·87	1·4060	71·7	2·81	—
145–200°	8·26	0·7868	1·4460	4·9	30·0	2·47	1·4176	77·5	1·42	—
Above 200°	62·71	0·8200	1·4682	1·4	± 50·0	± 46·0	—	—	± 14·5	244·3
Distill. loss	0·30	—	—	—	—	—	—	—	—	—
							Total		±22·4	
Experiment 2.—Phenyl-octadecane at 470° C.; pressure at react. temp. 276 atm.; after cooling 82 atm.										
Hydrocarbon gas	24·55	—	—	—	—	—	—	—	—	—
Hydrogenation loss	6·20	—	—	—	—	—	—	—	—	—
Charcoal absorb.	7·72	—	—	—	—	—	—	—	—	—
20–70°	16·28	0·6452	1·3702	1·9	10·0	1·62	1·3630	—	1·60	—
70–90°	5·68	0·7449	1·4230	2·0	33·5	1·90	1·3877	64·0	1·88	—
90–115°	10·52	0·7638	1·4342	2·3	37·5	3·94	1·3970	65·4	3·30	—
115–145°	12·27	0·7997	1·4558	1·9	54·0	6·62	1·4079	69·5	4·81	—
145–200°	8·87	0·8196	1·4648	1·9	47·5	4·21	1·4201	74·5	2·42	—
Above 200°	7·05	0·8713	1·4964	2·3	51·0	3·59	1·4336	87·5	1·56	177·0
Distill. loss	0·86	—	—	—	—	—	—	—	—	—
							Total		15·57	
Experiment 3.—Phenyl-octadecane at 490° C.; pressure at react. temp. 300 atm.; after cooling 82 atm.										
Hydrocarbon gas	54·63	—	—	—	—	—	—	—	—	—
Hydrogenation loss	9·50	—	—	—	—	—	—	—	—	—
Charcoal absorb.	4·33	—	—	—	—	—	—	—	—	—
20–70°	4·82	0·6440	1·3728	1·2	10·0	0·48	—	—	0·47	—
70–90°	9·55	0·8021	1·4553	1·2	58·0	5·54	1·3968	52·4	5·47	—
90–115°	5·68	0·8362	1·4775	1·1	78·5	4·45	1·4097	55·4	3·73	—
115–145°	7·10	0·8572	1·4905	1·1	92·5	6·56	1·4185	—	4·76	—
Above 145°	3·29	0·9225	1·5266	—	86·0	2·82	—	—	1·42	152·9
Distill. loss	1·10	—	—	—	—	—	—	—	—	—
							Total		15·85	

Experiment 4.—n-Octadecane at 440° C. Result: Gas and 85·6 per cent. liquids. All reaction products are paraffins with about 2 per cent. unsaturateds.
Experiment 5.—n-Octadecane at 490° C. Result: Mainly gas and 12·65 per cent liquid boiling 10–150° C. All reaction products are paraffines.
Experiment 6.—Toluene at 490° C. Result: Gas and 84 per cent. liquids boiling 44–115°. Composition on initial material: about 50 per cent. toluene, 25 per cent. benzene, 5 per cent. naphthenes.
Experiment 7.—Benzene at 490° C. Result: About 96 per cent. unchanged benzene and 3·5 per cent. naphthenes.

arrangements is given by Ipatiev,[6] Orloff and Lychatcheff[7] and Szayna.[8]

Experiment No. 3 at 490° C. showed a very large decomposition, and about two-thirds of the phenyl-octadecane was split to gas. The hydrogenation reaction of phenyl groups has not been carried above 470° C., and approximately 15·85 per cent. of phenyl groups were found in the reaction products. Possibly the equilibrium of hydrogenation is displaced at 490° rather unfavourably as compared with 470°, but unquestionably the deficiency of hydrogen has here also played an important rôle. Although in all the experiments large amounts of hydrogen (10 per cent. by weight) were used, and at lower temperatures this excess was sufficient to secure a suitable hydrogenation, at 490° on account of multiple scissions, this amount appeared to be too low.[9] The gas released from the autoclave after the reaction revealed only a small content of hydrogen, therefore it may be assumed that its partial pressure was too low for hydrogenation of nuclei.

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Laboratory of Petroleum Technology,
Polytechnic School in Lemberg, Poland.

[6] Cyclohexane to methyl-cyclopentane: Ipatiev and Dowgilevitch, *Ber.*, 1911, **44**, 2987.

[7] Decahydro-naphthalene to methyl-hydrindene: Orloff and Lychatcheff, *Ber.*, 1930, **63**, 2179.

[8] Diphenyl to methyl-cyclopentane: Szayna, Przemysl, *Chem.*, 1932, **10**, 221; Petroleum, 1933, **29**, (46), 15.

[9] Each scission of the carbon bonds necessitates, under conditions of high pressure hydrogenation, the saturation with one hydrogen molecule; hence, by many scissions, a correspondingly large amount of hydrogen is absorbed.

Oxidation under Pressure. Transformer Oils.*

By L. P. Chebotar, Ph.D.

Summary.

1. A method is described for the comparison of transformer oils by oxidation under pressure of oxygen at 151° C.
2. Oxidisability is expressed in mgr. of oxygen consumed per 100 ml. in a given time (2, 4, 6 hrs.).
3. A series of anti-oxidants was found for Nujol, but none for transformer oils.
4. Calibration of the bomb is described.
5. Testing the bomb for leakage is discussed with reference to its prevention.
6. Michie and Sligh methods are found unsuitable for testing oxidisability of oils.

Auto-Oxidation.

The literature on auto-oxidation may be divided into three periods connected with the names of :—

1. Schönbein.
2. Bach and Engler.
3. Moureu.

1. Schönbein,[23] the discoverer of ozone, regarded auto-oxidation of organic compounds (ether, turpentine, essential oils, etc.) as related to "activation" of oxygen (formation of ozone). An odour of ozone emanating from oxidising substances was responsible for the hypothesis. Brodie,[5] Clausius,[11] Loew,[21] Hoppe-Seyler,[17] Baumann,[2] Van't Huff,[24] and Jorissen[20] were among the supporters of the hypothesis of activation of oxygen for explanation of auto-oxidation which usually proceeds with acceleration, although ozone was not found in auto-oxidation of organic substances.

2. Bach[1] was the first to recognise peroxide formation as a first step in auto-oxidation. Engler[13] devoted a great amount of research to the support of the peroxide theory of Bach. He proved in many cases that the first step in auto-oxidation is the formation of peroxides, which often have a pungent odour reminiscent of ozone, and that ozone is not evolved in the process of the auto-oxidation of organic substances. Engler confirmed the "peroxide" theory of Bach and dismissed the theory of "activation" of oxygen of Schönbein.

3. The accuracy and fastidious cleanliness characteristic of the work of Moureu[22] enabled him to discover anti-oxidants and accelerators in auto-oxidation, and to explain the phenomena which were baffling Engler in his attempts to measure the auto-oxidation of turpentine, using K I as an acceptor of active oxygen. Mouren showed that K I, as well as many other iodine compounds, are good anti-oxidants.

* Paper received November 18th, 1933.

In order to appreciate the extraordinary measures which Moureu took to avoid contamination, it is necessary to consult his work in the original (*Ann. Chimie*, 1921, 157-211, and *Bull. Soc. Chim.*, 1924, 1564-1607). The work of Moureu greatly stimulated research on auto-oxidation of organic substances. This resulted in a considerable literature on anti-oxidants and their application in various industries. Many anti-oxidants discovered by Moureu have been patented by others for various industries, quite often by "blanket patents." The work of Moureu and of Dupont[12] points to difficulties in auto-oxidation research due to casual contamination of substances or surroundings. This is especially true in technical research dealing with complex and varied mixtures. Therefore, any industrial research on auto-oxidation must be preceded and accompanied by research with c.p. chemical substances of suitable classes.

Standard methods of testing oxidisability of transformer oils (Michie and Sligh) are indirect methods. They measure the degree of oxidation by the amount of sludge formed instead of by direct measurement of the oxygen consumed. Paraffin base and naphthene base oils differ in their oxidation products. The latter will give more asphaltic products, while oxidation products of paraffin oils will contain a larger proportion of acids, etc. Herein lies the difficulty of comparison by Michie or Sligh tests of oils from widely different crudes. The oil might oxidise as easily as paraffin (Nujol, Adhesine, etc.), but according to Michie or Sligh tests, it might be classed as "very resistant."

Direct measurement of oxygen consumed in the oxidation of transformer oils was undertaken by two investigators, Butkov and Evers. Butkov[7] oxidised transformer oils (25 ml.) at 150° C., and 14 atm. of oxygen in an enamelled calorimetric bomb, supplied with a gauge for measurement of the oxygen consumed. In later articles, Butkov abandoned direct measurement of the oxygen absorbed and changed to indirect methods, first to the measurement of saponification[8] and later to the measurement of sludge formed in four hours at 150° C. and 15 atms. oxygen.[9]

Evers[15] oxidises oil (15 g.) mixed with a catalyst (60 g.) at 100° C. and atmospheric pressure. The catalyst is prepared by precipitation of Cu or Fe oxides on silica gel. The oxygen absorbed is measured electrically and expressed in amperes. While not going into further details of Evers' method, the writer objects to the use of solid catalysts in standard methods for testing oils. According to the experiences of the writer (which are in agreement with those of many others), solid catalysts are variable, and one cannot be sure that two batches of the catalyst deposited on silica gel would be identical (standard).

Review of Bombs.

Searching the literature on pressure vessels from time of Regnault, etc., the writer found much instructive reading, but nothing more suitable for his purpose than the old Berthelot tomb.[4] Later calorimetric bombs tend only to commercialise the original Berthelot bomb. Mahler substitutes heavy platinum lining with an enamel; Parr, with Illium; Roth, with Krupp stainless steel, etc. The only bomb considered by the writer besides a calorimetric bomb was the bomb of Cailletet,[19] constructed for liquefaction of gases and extensively used by many for high pressure experiments.

Bergius[3] adopted Cailletet's construction for his experiments on hydrogenation of coal, etc. Cailletet bombs differ from calorimetric bomb in that the cover is tightened to the bomb by a hollow plug screwed inside of the bomb instead of a wider nut screwed on the outside cylinder of the bomb.

Ipatief's[19] bomb is of flanged type and seemed to the writer to be too wide and heavy, but otherwise is a model apparatus for work under pressure. Fisher's[16] autoclave with shaking device is a small manufacturing rather than a fine physical apparatus, where every milligram of oxygen must be accounted for.

Ernst[14] gives a series of designs of equipment for high pressure reactions from his experience with synthetic ammonia.

Hunn, Fisher and Blackwood[18] make use of a calorimetric bomb construction for their oxidation of gasoline under pressure. Zublin[25] uses a flanged bomb with light walls which looks rather hazardous after many explosions reported in connection with testing gasolines under pressure of oxygen.

Apparatus.

The apparatus used by the writer was originally designed (December, 1928) for research on cracked gasoline. It consists of a bomb made of monel metal capable of withstanding 80,000 lb. pressure and supplied with a gauge and valve for admitting oxygen under pressure. It has three joints all tightened on antimony-lead gaskets.

Operation.

A test tube with 50 ml. of an oil such as transformer oil is placed in the bomb and covered with a glass cover. Then the bomb is closed, filled with oxygen to 300 lb. pressure and set into the boiling methyl-phenyl ether bath. The pressure is observed and noted every 10 min. until maximum pressure is reached and passed. Then the pressure can be noted once in half an hour.

[*Note.*—It is useful to set the bomb into the boiling bath by stop watch and to note pressure in first minutes (1, 2, 4, 7 and 10).

By the character of the curve in 10 or 20 min. can be judged if the bomb is tight or if it leaks.]

The experiment should be continued for 5 to 6 hrs. for transformer oil and might be finished sooner for more oxidisable oils. When the experiment is finished the bomb is placed in cool water. The oxygen should be released while the bomb is still warm. If the oxygen is released abruptly or the bomb is cooled too long or not cooled at all, the oil will bubble through the valve and it becomes necessary to take the gauge and valve off and wash them with ether.

[*Note.*—Gauges are usually delivered full of oil, and it is necessary to wash this oil off with ether before using the gauge.]

The test tube is washed with benzole-acetone (1 : 4) first, then generously with water, followed with chromic mixture, and then very generously with warm water, finished with distilled water and placed in a drying oven at 100° C. It must be ascertained that no visible traces of gum remain in the glass tube before setting it into the drying oven. The tube must be well examined again after it is taken from the drying oven.

Calibration.

The drop of pressure observed on the gauge can be calibrated in milligrams of oxygen consumed per 100 ml. of the oil. A Hempel gas burette with two-way stop cock has been used for this purpose.

The test tube with 50 ml. of an oil was placed in the bomb and the latter filled with oxygen up to 300 lb., as for testing oxidisability of oils. The burette was connected to the valve of the bomb through a suitable union and a short piece of rubber tubing. The connections were thoroughly tested for perfect tightness. Then the valve was slowly opened until the burette was filled with oxygen. The drop of pressure on the gauge and the corresponding volume of oxygen in the gas burette were noted. In such a manner for the bomb used, it has been found that 1 lb. drop of pressure on the gauge corresponds to 2·4 ml. in the burette at 20° C. or 3·2 mgr. of oxygen.

From the calibration of the gauge at 20° C. we can pass to that of the gauge at the conditions of testing oxidisability of oils. The initial pressure of 300 lb. oxygen rises in the bomb to 480 lb. due to the expansion of the oxygen and of the oil on heating the bomb from 20° C. to 151° C. Therefore, 1 lb. drop of pressure under our conditions will correspond to :

$$3{\cdot}2 \times \frac{300}{480} = 2 \text{ mgr. oxygen.}$$

This has been calculated for 50 ml. of an oil, thus :

1 lb. drop of pressure on the gauge corresponds to the consumption of 4 mgr. of oxygen per 100 ml. of an oil.

Capacity of the apparatus:

Volume of the oil	50 ml.
Volume of the glass of the test tube	13 ml.
Free space	35 ml.
Total volume	98 ml.

The volume of the bomb proper was measured by water from pipettes as 85 ml. Therefore, the capacity of the gauge and the connections will be 98 - 85=13 ml.

The calibration of the gauge of the apparatus in mgr. of oxygen permits comparison of the results obtained with different bombs, glass tubes, gauges, etc. It also gives an opportunity of testing the gauges without disconnecting them from the apparatus.

Oxidisability of Various Oils.

In Table I. we have compared the oxidisability of transformer oils with that of paraffin wax and non-sludging oils. The three samples of the transformer oils differ little in oxygen absorbed

Table I.

Oxidisability at 151° C. and 480 lb. expressed in Milligrams of Oxygen absorbed per 100 ml. of Oil.

	Transformer Oils.			250 Red	Squibbs		Adhesine
	A.	B.	C.	Oil.	Medicinal Oil.	Nujol.	H. (Russian).
Time in min.—							
30	0	0	0	0	130	210	250
60	0	0	4	20	310	320	350
90	2	0	8	40	470	480	520
120	7	8	14	64	590	600	640
180	16	20	28	68	—	—	—
360	57	66	68	220	—	—	—
Induction Period min. ..	150	135	120	50	12	12	25
Sp. Gr.	0·8718	0·9106	0·8961	—	0·8888	0·8855	0·8718
Iodine	15	13·8	11·1	15·7	0·17	0·65	—
Saponification	1·2	1·2	1·1	2·3	0·47	0·97	0
Sligh Test	18·5	32·5	16·2	58·7	0	0	0
Michie Test	0·15	1·9	2·1	0·83	0	0	0
Absorption by H_2SO_4 ..	3·3	6·7	3·3	13·3	1·7	1·7	—

in 6 hrs. Red oil absorbs about three times as much as the transformer oils. Still more oxidisable are Squibb's Medicinal Oil Nujol and Adhesine H (Russian non-sludging oil). It is of interest to note that the most oxidisable oils such as Adhesine H, Nujol and Squibb's show no sludging according to Michie or Sligh tests; therefore, Sligh and Michie tests are not suitable for testing oxidisability of oils. They show only the amount of insoluble sludge formed in oxidation of oils. Only direct determination of oxygen absorbed by oils can give a measure for oxidisability of oils and can claim to be a life test of oils.

Table II. shows the influence of various anti-oxidants on oxidisability of Nujol. The best anti-oxidant found is beta-naphthylamine. It prolongs the induction period 15 times and decreases the amount

of oxygen absorbed in 4 hrs. 60 times. The next best are beta-naphthol, alpha-naphthylamine and alpha-naphthol. Transformer oils also exercise antioxidant action on Nujol. Transformer oil A.

TABLE II.

Influence of Anti-oxidants on Oxidisability of Nujol expressed in Milligrams of Oxygen absorbed per 100 ml. of Oil

Time in Minutes—										
20	80	0	0	0	0	0	96	0	0
30	140	0	0	0	0	0	160	0	0
40	200	0	0	0	0	0	—	0	0
50	270	0	0	4	0	0	200	0	0
60	329	0	0	4	4	0	—	8	0
70	370	0	0	4	—	0	240	12	0
80	430	0	0	4	8	0	270	16	0
90	470	—	—	4	—	8	270	20	0
100	510	4	4	4	12	12	310	24	—
120	590	8	1	8	16	36	360	28	4
150	—	—	—	28	24	92	400	32	8
180	—	12	—	88	28	120	—	40	14
240	1000*	16	24	230	80	280	560*	48	20
300	—	28	96	400	240	390	—	64	28
360	—	56	310	520*	560	480*	—	80*	36
420	—	150	—	—	—	—	—	—	—
Induction Period in Min. ..	12	180	180	130	100	90	11	70	165
Anti-oxidant ..	—	1% Beta-Naphthylamine.	1% Beta-Naphthol.	1% Alpha Naphthylamine.	1% Alpha Naphthol.	1% Diphenylamine.	20% C.	Transformer Oil. B.	A.

* Extrapolated.

has double the action as compared with B. and 28 times as compared with C. This phenomenon might serve for comparison of transformer oils, which differ little if oxidised alone (see Table I., columns 1–3) and differ greatly if diluted with Nujol (1 : 4).

TABLE III.

Influence of Beta-Naphthylamine on Transformer Oils expressed in milligrams of Oxygen consumed by Oils.

Time in Minutes—	Transformer Oil. A.		Transformer Oil B.		Transformer Oil C.		Nujol.	
40	0	0	0	0	0	0	200	0
50	0	0	0	0	0	0	—	0
60	0	0	0	0	4	0	320	0
90	2	8	0	4	8	4	480	4
120	6	18	8	8	12	16	600	8
180	12	32	20	33	28	190	—	12
240	28	46	36	72	40	390	—	16
300	36	56	50	110	52	780	1000*	28
350	56	68	62	130	68	—	—	56
Induction Period in min.	150	100	135	135	120	110	12	180
Beta-Naphthylamine%	0	0·1%	0	0·1%	0	0·1%	0	0·1%

* Extrapolated

Table III. shows the peculiar action of beta-naphthylamine. For Nujol it acts as a good anti-oxidant, while with transformer oils it acts as an accelerator of oxidation. It is of interest to note that the accelerating action of beta-naphthylamine is parallel to that caused by the dilution of transformer oils with Nujol. Many other substances were tried as anti-oxidants. It has been found that diphenyl-amine is a good anti-oxidant for Nujol (but not for

transformer oils). Oleic acid and tetraline show slight anti-oxidant action for Nujol. Naphthenic acids and tin-oleate, as also higher alcohols (cetyl and myristyl) have no influence on oxidation of Nujol.

Silica *versus* Glass.

According to Brunner[6] the oxidation of benzaldehyde proceeds much more quickly in the presence of quartz powder than in the presence of glass powder. He even determined that the surface of quartz is about twelve times more active than that of glass. It was of interest to see whether quartz test tube would accelerate oxidation of hydrocarbon oils such as Nujol and transformer oils. Negative results were obtained. There is no difference in the speed of oxidation of Nujol or of transformer oils in quartz and Pyrex test tubes.

Induction Period.

Induction period or time required to start the oxidation of oils at 151° C. and 300 lb. initial pressure of oxygen (about 480 lb. maximum pressure) varies considerably for the same oil if an attempt is made to note the first sign of drop of pressure on the gauge. The beginning of pressure drop may be noticed with the first ½ lb. of drop of pressure, but sometimes the arrow of the gauge jumps 2 lb. in a second and then does not move further for a long time. Therefore, it is necessary to specify what drop of pressure shall be considered as a reliable sign of the beginning of the oxidation. After a series of experiments in checking the induction periods for oils a 3 lb. drop (or 12 mgr. of oxygen per 100 ml. of oil) was chosen as a reliable sign that oxidation has started, because below 3 lb. it is difficult to check the induction period as it varies.

Oxidation Number.

Oxidation number is expressed in milligrams of oxygen absorbed by 100 ml. of oil in a given time (2, 4, 6 hrs.). For comparison of easily oxidisable oils such as Nujol, Adhesine, etc., a 2 hr. test is sufficient (Table I.). For 250 Red Oil 4 hrs. are necessary. For transformer oils even 6 hrs. of oxidation do not seem sufficient. From the tables it will be seen that oxidation number gives a better measure of the oxidisability than the induction period.

Maximum Speed.

If the speed of oxidation is calculated for every 10 mins. of the experiment, it will be seen that the oxidation of all oils (or gasoline, etc.) proceeds first with an acceleration and then slows down. Therefore, maximum speed of oxidation can always be

determined. In order to be more reliable and not to depend on a casual jump of the gauge, maximum speed should be taken as an average over a period of time not less than 30 min. (or for a drop of pressure of not less than 30 lb.).

In Table I. can be seen that the maximum speed of oxidation of transformer oils does not exceed 15 milligrams of oxygen per 100 ml. in 1 hr. For 250 Red Oil the speed reaches 50 milligrams per hr., and for Adhesine 340 mgr. per hr. per 100 ml. of oil.

The oxidisability of the three oils is compared in three different ways in table below :—

	Transformer Oil C.	250 Red Oil.	Adhesine H.
Induction Period	.. 120	.. 50	.. 25
Oxidation Number (2 hr.) ..	.. 14	.. 64	.. 640
Maximum Speed of Oxidation..	.. 15	.. 50	.. 340

It appears that " Oxidation Number " best expresses oxidisability ; Maximum Speed of Oxidation being next best.

All three series of figures are obtained in the same experiment and all are useful criteria of oils. Further accumulation of data will show which series of figures is most important.

Leakage.

Leakage of the bomb is the most difficult problem in measuring oxidisability of oils (or gasoline) under pressure of oxygen at 150° C. (or 100° C.). It is very easy to make the bomb tight at room temperature so that it will hold pressure without any change for a week and more, but if the bomb is heated in water bath (or methyl-phenyl ether bath) the joints of the bomb relax and some " puffing off " of the oxygen can be noticed. By calculation of the pressure due to the expansion of the oil and of the oxygen, the smallest leakages can be detected and estimated.

If a special investigation for leakage is not made, leaks might be easily overlooked and cause illusions and errors. It was found that in the case of very small leaks at the start (" puffed off "), the bomb tightens in a few minutes and holds pressure well for hours. In case of larger leakages at the start the bomb tightens also and sometimes holds pressure well. Often, however, tiny insidious leaks, easy to overlook, remain.

The smoothness of the joints of the bomb, and especially the correctness and smoothness of the threads, are of the most importance in combating leakage. Washing threads with benzole and rinsing with tooth brush is necessary. Grinding threads and joints with oil often improve the tightness of the bomb. The last operation is a delicate one, and should be made by the chemist himself, because the polishing of the thread can be easily overdone with disastrous results.

It is easy to see that the leakage of the bomb in testing oxidisability of oils (or gasoline) influences the results a thousand times more than in the case of a calorimetric bomb. Therefore, the workmanship required for making the bomb for testing oxidisability of oils must be at least equal to that of the calorimetric bomb.

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